SELECTIVE HYDROGENATION OF A MULTIFUNCTIONAL COMPOUND: 2-BUTYNE-1,4-DIOL TO *CIS*-2-BUTENE-1,4-DIOL

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By

Bernard Cullen

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ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

Abstract

A 1% Pd/C catalyst supplied by ICI Synetix has been characterised, and used for the selective hydrogenation of 2-butyne-1,4-diol. The reaction procedure was developed for both an ambient and an elevated pressure reaction vessel, the hydrogenation of 2-butyne-1,4-diol was bench-marked with the 1% Pd/C catalyst. Two 1% Pd/Al_2O_3 catalysts have been prepared, characterised and used for the hydrogenation of 2-butyne-1,4-diol also. All three of the 1% supported palladium catalysts have been characterised with CO chemisorption, electron microscopy and BET surface area determination.

When the two 1% Pd/Al_2O_3 catalysts were employed for the selective hydrogenation of 2-butyne-1,4-diol, not only did they exhibit a different rate of hydrogenation of 2-butyne-1,4-diol, but also different final product distributions, with the selectivities towards formation of *cis*-2-butene-1,4-diol being of the same order (circa 95%) as that achieved when the 1% Pd/C catalyst was employed.

An unexpected compound for this type of catalytic hydrogenation called iso-propoxytetrahydrofuran was formed in all the reactions that employed the 1% supported palladium catalysts. Its formation occurred because of a solvent/bound surface species interaction, in a concerted ring closure process. Iso-propoxytetrahydrofuran has been isolated, purified, characterised with NMR and GC-MS and calibrated for GC analysis.

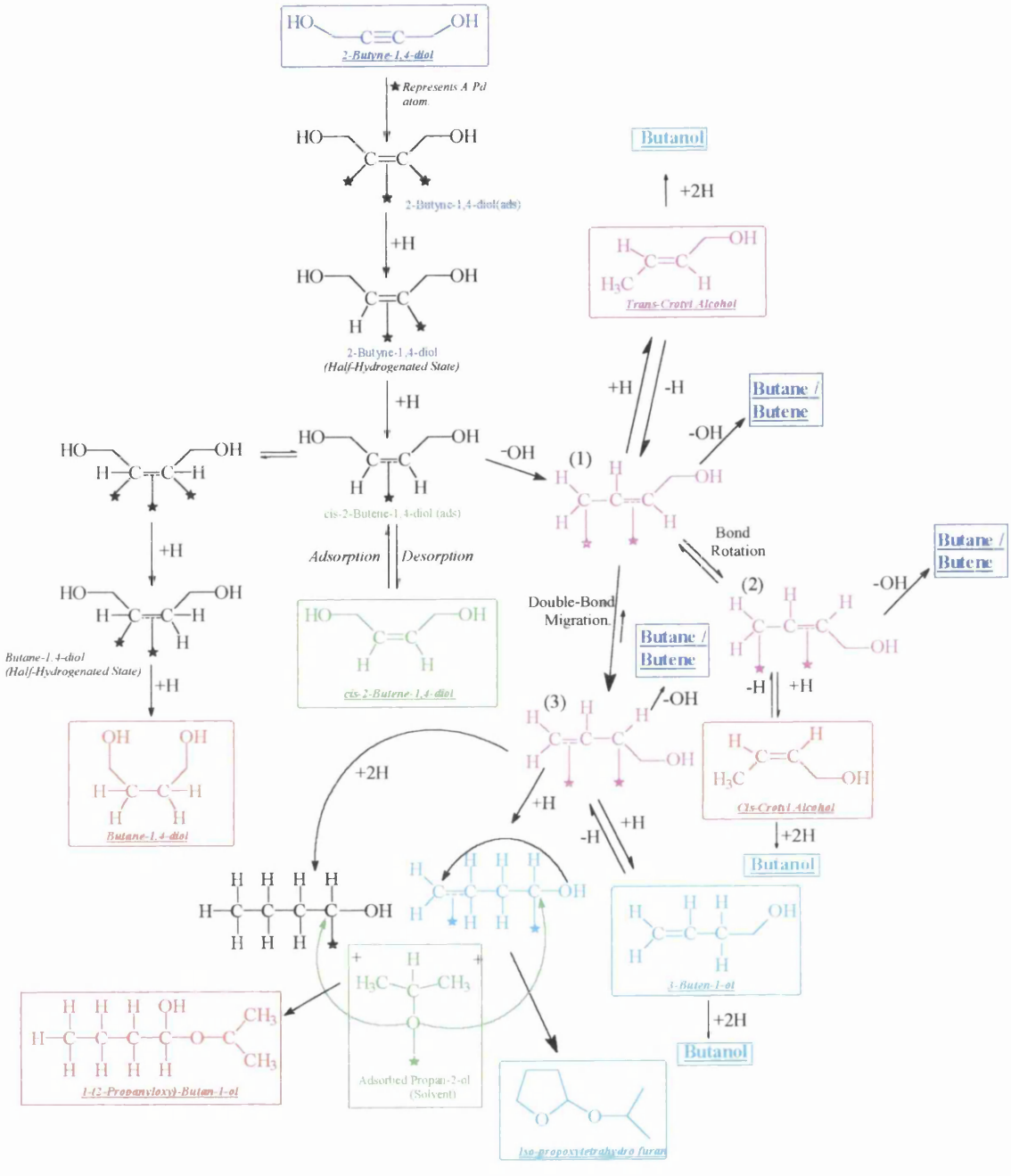
No iso-propoxytetrahydrofuran was formed when a 9.1% Cu/SiO_2 catalyst was employed for the selective hydrogenation of 2-butyne-1,4-diol. The 9.1% Cu/SiO_2 catalyst offered the advantage of a higher selectivity towards 2-butene-1,4-diol formation than any of the supported 1% palladium catalysts (circa 97%), but at a far slower rate of hydrogenation.

By changing the reaction solvent it was possible to produce different furans, and also have an impact of the rate of hydrogenation of 2-butyne-1,4-diol, the rate of hydrogenation in distilled water was around half of that observed when propan-2-ol was employed as the reaction solvent. With distilled water as the reaction solvent, hydroxy-tetrahydrofuran was produced during the course of the reaction, with *n*-butanol as the reaction solvent, butoxy-tetrahydrofuran was produced during the course of the reaction.

A series of experiments employing mono-substituted alkynes was conducted to try and elucidate the reaction mechanism for the selective hydrogenation of 2-butyne-1,4-diol. It was found from these experiments that a diol functionality was required on the reagent species for the formation of iso-propoxytetrahydrofuran to occur.

Targeted isotope switching experiments, in combination with ^{1}H and ^{2}D NMR spectroscopy and GC-MS were conducted so that all the experimental observations made during the course of the study could be consolidated into one postulated reaction mechanism. The postulated reaction mechanism derived from this study can be seen in Figure 1 below.

Figure 1: Postulated reaction mechanism



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Abstract

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Chapter One

INTRODUCTION

1.1 GENERAL INTRODUCTION

The history of catalysis is a long one. For almost two centuries catalysis has provided a focus for intrigue and interest for researchers. Dobereiner in 1823 founded the application of catalysis with the platinum catalysed reaction between oxygen and hydrogen [1]. The early work on catalysis was continued by Kirchoff, Henry, Philips, Davy, Faraday and Berzelius [2], by 1835 the existence of heterogeneous catalysis had been established. It was Jakob Berzelius who was the first to use the term "catalysis". Jakob Berzelius defined the power of the catalyst as being that which is able to "wake affinities, which are asleep at this temperature, by their mere presence and not by any affinity." It was not until 1875 the first large scale industrial use of a catalyst occurred. Which was the use of platinum catalysts in the formation of sulfuric acid through the contact process. Its inventor Peregrin Philips died before the fruition of his efforts was realised [3].

The interpretation of catalysis evolved with the subsequent studies that increased the knowledge and understanding of the field. But, as different approaches to catalysis have developed from different viewpoints, an universally-accepted, precise definition still remains problematic. C. N. Satterfield [4] has adopted this definition: *A catalyst is a substance that increases the rate of reaction towards equilibrium without being appreciably consumed in the process.*

Catalysis plays a very vital role in the modern chemical industry, most industrial reactions are of a catalytic nature. Catalysts are employed at some stage in the manufacture of a large percentage of chemical goods, all but a few of the countries in the world gross national product is exceeded by the value of the goods produced by the United States' chemical industries [5]. There is a vast amount of applications for catalysis, pharmaceutical, petrochemical, fine and heavy chemical industries, and these industries predominantly use heterogeneous catalysis in their processes.

1.2 CHEMISORPTION AND PHYSISORPTION

The initial and most important step of any reaction in heterogeneous catalysis is the adsorption of the reactant(s). In adsorption molecules of a particular material become attached or concentrated at an interface, with an interface describing the area between two distinct phases. Gas-solid, liquid-solid and gas-liquid are typical examples of interfaces. *Chemisorption* and *physisorption* are the two classifications of adsorption.

1.2.1 Physisorption (Physical Adsorption)

Van der Waals adsorption or physical adsorption involves weak and associative bonds between reactant and substrate. There are only small heat changes accompanied with this type of adsorption, they are often of the same order of magnitude as the heat of liquefaction of the adsorbing gas. The physical adsorption of a molecule at an interface is not directly associated with any distinct surface atom, and may occupy an area independent of the nature of the adsorbate, unlike in chemisorption. Since the forces involved between the adsorbate and the adsorbent are similar in magnitude to those involved between molecules in a liquid, physisorption is prone to multi-layer adsorption. The physisorption of oxygen on titania is a typical example, which involves a binding energy of approximately 5kJ mol^{-1}. This is not markedly different from the latent heat of condensation of oxygen (6.80kJ mol^{-1}).

Typical application that employ physical adsorption include the determination of catalyst surface area and pore structure characteristics through low temperature nitrogen adsorption; the boiling point of the adsorbate being close to the temperature at which the adsorption occurs. These procedures allow correlations to be drawn between the behaviour and structure of the catalyst under reaction conditions.

1.2.2 Chemisorption (Chemical Adsorption)

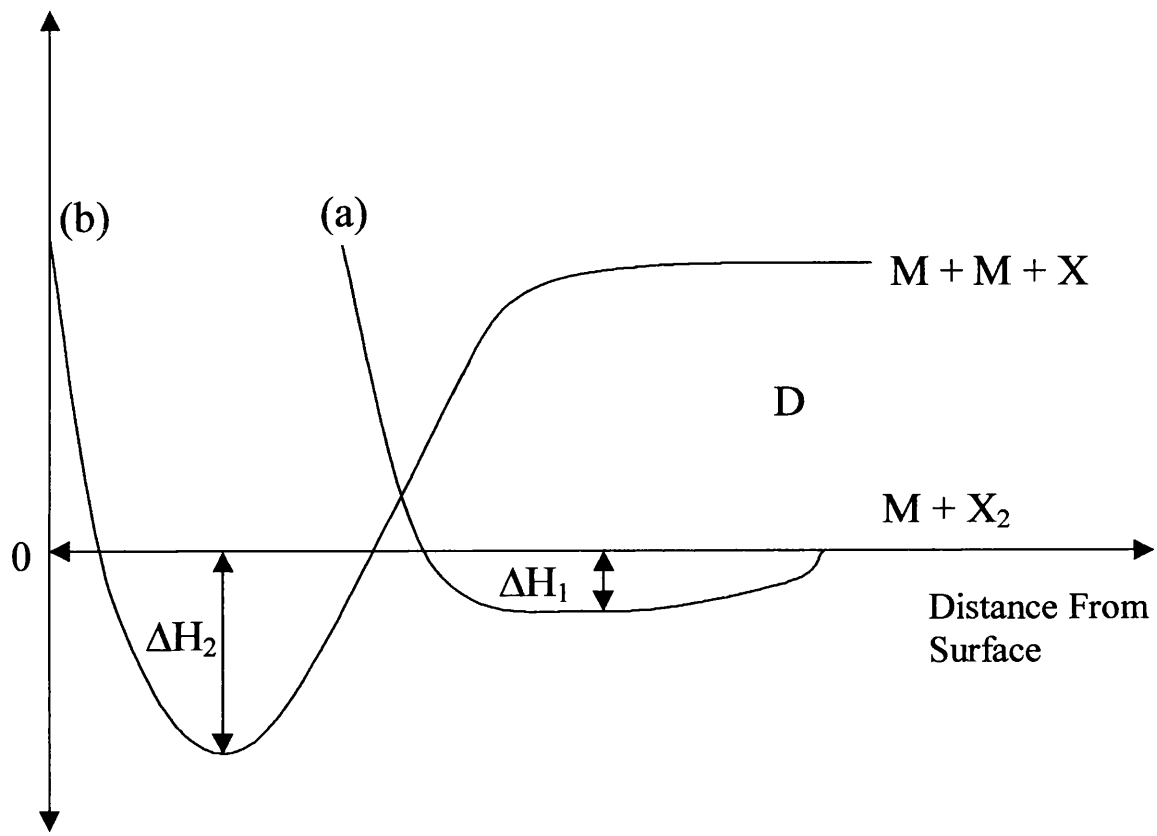
In chemical adsorption (chemisorption) the adsorbate molecules are held at the surface by valence forces that are similar to those present between atoms in a molecule. This can be observed between an adsorbing gas and a metal surface, where the metal possesses unoccupied orbitals, which provide sites for co-ordination. There are much stronger chemical bonds formed during chemical adsorption than those formed during physical adsorption. The heats involved during chemical adsorption are similar to those liberated during chemical reactions. The reactivities of molecules may be altered upon surface adsorption, and may be greatly enhanced, if you consider the energy changes observed in chemisorption processes. When chemisorption is accompanied by the dissociation of the adsorbate, this is indeed the case. If you the adsorption of hydrogen on tungsten, where the (H-H) bonds are broken, the resulting dissociated hydrogen atoms are more reactive than the free hydrogen molecules. For catalytic reactions, the chemisorption of at least one of the reactants is required to further reaction. There are a number of special features of chemisorption listed below;

i) adsorbate surface coverage never exceeds a monolayer
ii) there are often appreciable activation energies associated with chemisorption processes
iii) chemisorption can occur over a wide range of temperatures
iv) there is considerable variation in the adsorptive capacities of various surface sites observed

Figure 1.2.2 show the distinction between physical and chemical adsorption. If we consider the diatomic molecule X_2, physisorption of the molecule is represented by curve (a). The potential energy falls to a minimum as the molecule approaches the surface, this is represented by ΔH_1. The heat of physisorption can be assumed to be low, so this value will typically be small be. Curve (b) represents the chemisorption of the molecule at the surface. When the adsorbate molecules are separated by an infinite space from the

surface, they still possess energy D, this represents the molecular dissociation energy in the case of molecules that are prone to dissociation on adsorption. There is a decrease in the potential energy to a low minimum as the molecule approaches the surface. The molecule is much closer to the surface at this point than in physisorption. The term ΔH_2 is applicable to define the heat of chemisorption, because of the formation of new chemical bond between both the surface and adsorbate.

Figure 1.2.2: Distinction between physical and chemical adsorption



1.3 HYDROGENATION

Hydrogenation is the addition of hydrogen to a molecule, it is of estimable importance in chemistry. Hydrogenation can be employed to reduce functional groups, often with good selectivity. Hydrogenation can be applied using both homogeneous and heterogeneous processes, the latter is favoured as the reaction product(s) are more easily separated from the solid catalyst [6a].

Primarily nickel or palladium catalysts are employed industrially for catalytic hydrogenation [7], although other metals such as zinc, platinum, and copper are also employed. Various physical forms of catalyst can be employed, such as gauzes, wires and finely divided metal powders, but catalysts are most commonly prepared when supported on a high surface area oxide.

The choice of a catalyst is determined by three important factors; *selectivity*, *activity* and *lifetime* [8]. The selectivity reflects the ability of the catalyst to form the desired product, the activity is the rate at which the catalyst can convert the reactant to product(s). The lifetime is the period for which the catalyst maintains an acceptable level of activity and/or selectivity. The cost of the catalyst manufacture and any associated toxicity hazards must also be considered. These are the factors that predominantly govern catalyst selection for an industrial process; the ultimate choice is usually made in economic terms.

1.4 HYDROGENATION OF ALKYNES

The selective hydrogenation of alkynes to achieve partial hydrogenation and, therefore produce alkenes is of fundamental importance [9]. In some basic chemical processes there is the requirement for reagent grade purity of alkene with a very low concentration of alkyne impurity. This aim can normally be met by the application of supported metal catalysts, typically low loaded

Pd/Al_2O_3 which can be used to selectively reduce the alkyne impurity to the desired olefin [10, 11].

Catalytic hydrogenation is widely employed in both laboratory practice and fine chemical production for the selective synthesis of alkenes [12, 13]. Catalytic hydrogenation is also a crucial step in industrial polymerization processes with the aim of complete elimination of alkynes in the alkene feedstocks. Examples of this are the selective removal of propyne from a propylene-rich stream (C3 hydrorefining) and the selective hydrogenation of acetylene in a ethylene-rich stream (C2 hydrorefining), to avoid poisoning of the polymerization catalysts [9]. Naturally, high propylene and ethylene yields, respectively, are required without hydrogenating the existing alkene.

C2-C4 alkenes and reactive intermediates, such as vinyl chloride, propylene oxide, ethylene oxide and acrylonitrile are some of the most important building blocks in the modern petrochemical industry [9]. The world production of ethene just reached 1 million tons per year in 1950 [14]. The production reached 80.5 million tons in 1998, this underlines the importance of this chemical [15, 16]. One of the fastest growing commodity thermoplastic resins is polyproplene, this creates a strong demand for propylene. The world capacity for propylene production reached 47 million tons in 1998, and the global production of polypropylene (in 1996) was already 22 million tons [17]. There is an annual growth in demand for ethylene of 3.5%, and more than 5% for propylene. This will lead to a predicted worldwide demand of 120 and 82 million for ethylene and propylene respectively by 2010.

The high demands for high grade products either directly derived from catalytic hydrogenation of acetylenes, or derived from intermediates that have been produced employing catalytic hydrogenation, underlines the continued interest in developing more selective catalysts. There is still intense research activity to try and provide a better understanding of the factors that are decisive in determining catalytic selectivity. Selective hydrogenations have been extensively covered and studied in review papers [18, 19, 20, 21, 22, 23, 24, 25, 26] and books [6b, 27, 28, 29, 30] since the 1960s.

Ethyne hydrogenation has been well documented over the years [31, 32, 33, 34, 35, 36, 37]. There has been less work however on the selective hydrogenation of substituted alkynes reported [12]. Some of the studies that consider propyne hydrogenation are; with static reaction experiments [38], pumice supported and unsupported platinum and iridium catalysts [39], in a pulse-flow system employing a Pt/SiO_2 catalyst [40] and reactions performed in both a static and pulse flow system [41]. Studies conducted using 1-butyne [42, 43] and 2-butyne [44, 45, 46] have also been performed.

1.5 FINE CHEMICAL PRODUCTION

There are many, very different groups of products such as dyes, pharmaceuticals, food additives, photochemicals, cosmetics and vitamins are classified as fine chemicals. Many intermediates and products are produced by catalytic hydrogenation under mild conditions [47, 48]. The starting materials often have high molecular masses and complex structures, and are often temperature-sensitive. Most of these chemicals are hydrogenated in solution for this reason. Possible processes are reactions on fixed-bed catalysts and suspension processes with powder catalysts; a decisive role is often played by diffusion control.

The most important reaction in the production of fine chemicals is the selective hydrogenation of double bonds [49]. It is possible for hydrogenations to give rise to several different products, since the starting materials often have several reactive (functional) groups. With careful adjustment of all experimental parameters, including solvent, type and amount of catalyst, pressure, temperature and degree of mixing (e.g. stirring speed), it is possible to maximise the yield of the desired product.

The reactivity of some unsaturated groups can differ so much that selective hydrogenation is readily possible. The selective hydrogenation of 2-butyne-1,4-diol can be considered as a generic model for a fine chemical process.

1.6 HYDROGENATION OF 2-BUTYNE-1,4-DIOL TO *CIS*-2-BUTENE-1,4-DIOL

There is frequent application in the fine chemicals and pharmaceutical synthesis of the solid-catalysed reaction of a gas with a liquid that is often carried out in a slurry reactor. The selective hydrogenation of acetylenic compounds to form higher value products is a typical example. Of scientific and economical concern is the selectivity of the net formation of the intermediate compounds in these reactions. The selectivity towards the formation of a certain desired compound can be significantly effected by a number of factors. Even small variations in the amount of hydrogen adsorbed, by additives that change the rate of mass transfer relative to the rate of hydrogenation, the rate of olefin hydrogenation relative to that of the acetylene, and also by reaction variables such as temperature, concentration of catalyst, agitation, solvent and catalyst support [50].

A common situation involving a multifunctional hydrogenation is the hydrogenation of 2-butyne-1,4-diol to *cis*-2-butene-1,4-diol. The reduction of triple bonds is very selective over palladium [12, 50, 51, 52]. Due to its use as a chemical intermediate in the production of several insecticides and pharmaceuticals (e.g. vitamin B6 and endosulfan), there is a great deal of interest in butenediol.

There have been a number of different catalysts that have been employed for the selective hydrogenation of 2-butyne-1,4-diol. The use of nickel [53, 54, 55], Raney nickel [56, 57], Ni-Cu alloy [53] or supported palladium catalysts [50, 58, 59, 60, 61, 62, 63, 64, 65, 66] have been reported for this reaction under relatively mild conditions. The hydrogenation of 2-butyne-1,4-diol has

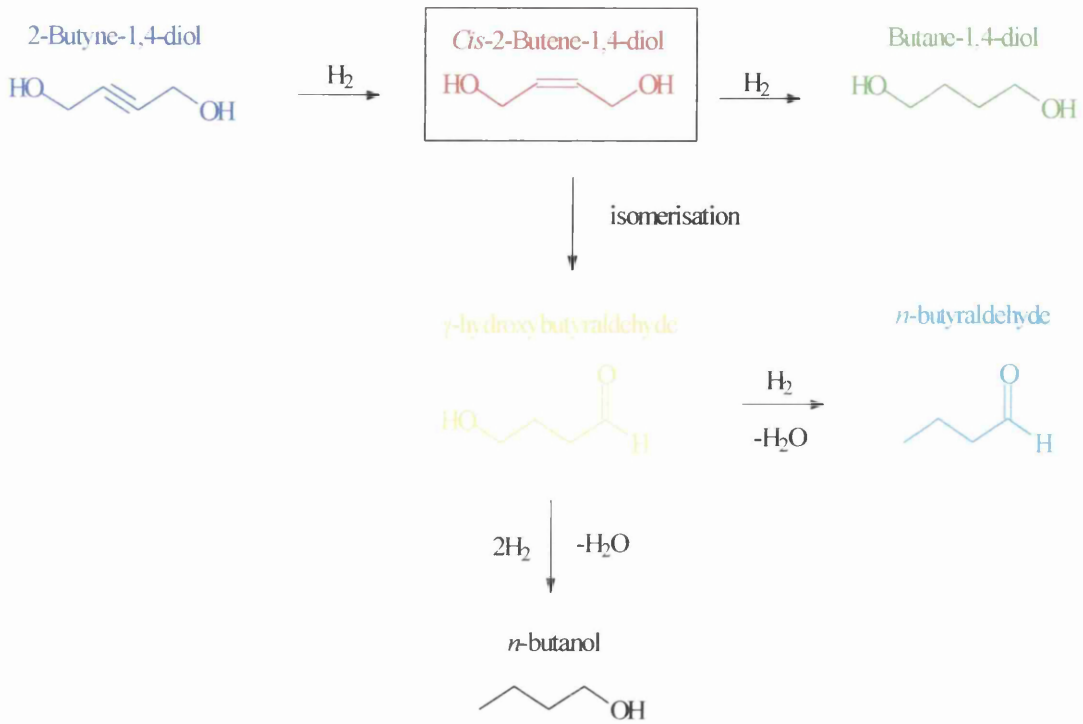
been looked at using several different solvents, methanol [67, 68, 53, 54, 64], water [50, 52, 55, 57, 58, 59, 60, 65, 66, 69, 70], pyridine [71], propan-2-ol [50], with different solvents having an effect on the selectivity of the reaction.

There have been a number of studies that have used catalytic poisons to try to improve selectivity of the catalyst. Winterbottom *et al* reported the use of various additives to try and improve the selectivity of the hydrogenation of 2-butyne-1,4-diol to *cis*-2-butene-1,4-diol [50]. Chaudhari [58] *et al* reported the use of a Lindlar catalyst that was doped with zinc acetate that gave partial reduction with a selectivity as high as 99.8% to *cis*-2-butene-1,4-diol formation. Fukuda and Kusama [66] employed a $Pd/CaCO_3$ catalyst using quinoline as a poison to sucessfully partially hydrogenate butynediol. A combination of quinoline and lead acetate was used in later work by Fukuda [65] on $Pd/BaCO_3$ to gave partial hydrogenation of butynediol as well. There is the possibility of several side reactions, because of this selectivity towards *cis*-butene-1,4-diol becomes important [50]. It has been reported that over Pd/C that the formation of butane-1,4-diol during the course of the first step, *i.e.* 2-butyne-1,4-diol to *cis*-2-butene-1,4-diol indicated the possibility of a sequential reaction without preferential formation and/or desorption of desired intermediate product. During the first reaction step *cis*-butene-1,4-diol and butane-1,4-diol were formed, side products such as γ-hydroxybutryraldehyde, *n*-butanol and *n*-butyraldehyde were also formed in small quantities during the first step and in significant quantities at complete reduction stage [59]. Butane-1,4-diol is produced on complete hydrogenation of the of 2-butyne-1,4-diol, which is a valuable commodity for the manufacture of synthetic rubber according to the Reppe process [52, 72] and of THF [52].

Telkar *et al* [60] has proposed a general reaction scheme (similar to the one proposed by Winterbottom *et al* [50]), employing a range of 1% supported palladium catalysts poisoned with NH_3, for the reaction (Figure 1.6). The scheme consisted of two stages. The first stage involved the adsorption and reduction of 2-butyne-1,4-diol to produce *cis*-2-butene-1,4-diol. This followed a consecutive mechanism. The second stage of the reaction involved the

production of butane-1,4-diol and a range of other side-products. This stage followed a sequential mechanism. The "side products" reported by Telkar *et al* were γ-hydroxybutyraldehyde, *n*-butyraldehyde and *n*-butanol.

Figure 1.6: Telkar *et al* proposed reaction scheme [60].



Previous investigations reported production of *n*-butyraldehyde as a result of 2-butyne-1,4-diol hydrogenation [52, 59, 60]. Formation of the side-product was reported once *cis*-2-butene-1,4-diol was able to react on the catalyst surface (*i.e.* after 100 % conversion of 2-butyne-1,4-diol). Butyraldehyde was reported to be formed in conjunction with *cis* and *trans*-crotyl alcohol, and *n*-butanol by Winterbottom *et al* [50]. Further discussion about 2-butyne-1,4-diol hydrogenation can be found in other chapters were relevant.

1.7 FURANS SYNTHESIS AND HYDROGENATION

Furans occur widely throughout nature in a variety of commercially important compounds [73]. There include pharmaceuticals (anti-inflammatory properties) and flavour and fragrance enhancers [74, 75]. Furans often play an important role as intermediates in synthetic pathways because they react as a special class of vinyl ethers [76]. They can also act as dienophiles in the Diels-Alder reaction [77]. It is not surprising that many methods have been devised for the syntheses of these derivatives given furans well documented uses, and the considerable synthetic challenge of many furan-containing natural products [73].

The synthesis of furan and many substituted furans can involve long complicated processes, many of these processes involve using strong acids and elevated temperatures [78, 79, 80]. The oxidation of alkynyl sulphones followed by treatment with strong bases to form poly-substituted furan molecules is a typical example [81]. If the production of such molecules could be achieved by selective hydrogenation of a single, substituted furan molecule, it would be more practical and cost effective. The selective reduction of 3-(2-furyl) acrolein over various supported catalysts is a typical example of such a process [82].

A furan undergoes hydrogenation and/or hydrogenolysis depending on which metal is used to catalyse the reaction. Palladium, rhodium and ruthenium tend to favour hydrogenation of the furan ring without cleavage [83]. Platinum, ruthenium, osmium and iridium and tend to favour hydrogenolysis of the ring [83]. Deactivation has been reported as a problem whilst using palladium catalysts for furan hydrogenation in the gas phase. The reason for this was carbon deposition [84, 85]. However, at 100°C and 20 bar, furan hydrogenation to THF occurs over palladium [85].

Extensive study has been carried out into the selective hydrogenation of 3-(2-furyl) acrolein, which is a highly substituted furan [82, 86]. This molecule

contained a substituent group at the two-position of the furan ring. The substituent group consisted of a ketone group and an olefinic bond. Over nickel catalysts a whole range of reduced molecules was produced, including molecules with saturated rings. There was very little hydrogenolysis observed [82]. The reaction was selective towards reduction of the carbonyl group and double bond, whilst leaving the furan ring intact, when palladium was employed [86].

Given the wide range of reactions and different syntheses that furans can be involved in, a relatively facile, high yield way of producing furans is of great interest.

Chapter Two

OBJECTIVES OF STUDY

Objectives of Present Study

One area of heterogeneous catalysis that is showing much interest is the selective hydrogenation of multifunctional compounds. The fine chemical industry is increasingly applying heterogeneous catalysis in the production of fine chemicals. The stereoselective hydrogenation of 2-butyne-1,4-diol to cis-2-butene-1,4-diol is an example of selective multifunctional hydrogenation. 2-butyne-1,4-diol is employed as a chemical intermediate in the production of insecticides and pharmaceuticals (e.g. endosulfan and vitamin B6). The selective hydrogenation of 2-butyne-1,4-diol is to be used as a guide for the suitability of different supported metal catalysts in the hydrogenation of multifunctional compounds. A number of the studies in the literature that investigate the selective hydrogenation of 2-butyne-1,4-diol have tended to look at the use of additives or selective catalyst poisons to try and increase the selectivity towards *cis*-2-butene-1,4-diol formation, this present study has not used and additive or selective catalytic poisoning to try and enhance the selectivity towards 2-butyne-1,4-diol formation.

The central aim of the present study, therefore, was to investigate the catalytic behaviour of a series of supported palladium catalysts and a supported copper catalyst for the ambient pressure and elevated pressure liquid phase hydrogenation of 2-butyne-1,4-diol. The goals for the project can be subdivided into objectives i) to iv).

i) Develop the necessary apparatus and protocol to allow the evaluation of the catalytic performance of palladium-based catalysts for the liquid phase hydrogenation of 2-butyne-1,4-diol at ambient and elevated pressure, using propan-2-ol as a solvent.

ii) Benchmark the selective hydrogenation of 2-butyne-1,4-diol using a 1% Pd/C catalyst supplied by ICI Synetix.

iii) Investigate the hydrogenation of selected other reagents and the selective hydrogenation of 2-butyne-1,4-diol in water to aid understanding of the reaction processes that occur during the selective hydrogenation of 2-butyne-1,4-diol in propan-2-ol.

iv) Employ D_2 gas, ^1H and ^2D NMR, and GC-MS to perform mechanistic studies of the selective hydrogenation of 2-butyne-1,4-diol, to aid in the formulation of an overall postulated reaction mechanism.

Chapter Three

EXPERIMENTAL

3.1 INTRODUCTION

Three of the four catalysts used in this study were prepared at Glasgow University using a wet impregnation method of preparation. Dr. Lennon's group prepared the two Pd/Al_2O_3 catalysts. The Cu/SiO_2 catalyst was prepared by D. Anderson for the liquid phase hydrogenation of Nitrobenzene [1]. The Pd/C catalyst, was also prepared a wet impregnation technique and was supplied by ICI Synetix.

Catalyst characterisation was performed on all four samples, this included transmission electron microscopy (TEM), surface area determination (BET) and chemisorption. The results of these characterisation procedures are given in the results chapter (in Section 5.1). The characterisation data for the Cu/SiO_2 catalyst can be found in D. Anderson's PhD thesis [1].

3.2 PREPARATION OF CATALYSTS

3.2.1 Metal precursors and supports

Two alumina-supported catalysts were prepared using a wet impregnation method. The metal salts supplied by Fluka were palladium (II) chloride ($PdCl_2$, 99.9+% purity), and palladium (II) nitrate ($Pd(NO_3)_2$, 99.9+% purity). The support that was used in the preparation of the two catalysts was Aluminium Oxid C, which is a γ-alumina supplied by Degussa. The preparation of the palladium chloride and palladium nitrate catalysts are detailed in a) and b) respectively below.

3.2.2 Preparation

a) Palladium chloride/Aluminium Oxid C

50g of the Aluminium Oxid C was weighed into a round bottom flask in a funehood. The flask was then placed on a stirrer plate and stirred slowly, while 250mls of distilled water was slowly added to the flask to form a slurry. A solution was prepared that has 0.84g of palladium chloride (4.75×10^{-3} moles of $PdCl_2$) to give a nominal metal loading of 1%. To this solution concentrated HCl was added dropwise to dissolve the palladium chloride. Once fully dissolved, the metal salt solution was added dropwise to the alumina slurry. The slurry was left to stir for 24 hours, after which any remaining water was removed using a rotary evaporator. The catalyst was then put in an oven and left to dry. Once the catalyst was dry it was ground and graded by particle size; retaining the fraction between 250 and 500μm to be calcined. The calcined catalyst was then used for reaction testing.

a) Palladium nitrate/Aluminium Oxid C

50g of the Aluminium Oxid C was weighed into a round bottom flask in a funehood. The flask was then placed on a stirrer plate and stirred slowly, while 250mls of distilled water was slowly added to the flask to form a slurry. A solution was prepared that has 1.09g of palladium nitrate (4.75×10^{-3} moles of $Pd(NO_3)_2$) to give a nominal metal loading of 1%. Once fully dissolved, the metal salt solution was added dropwise to the alumina slurry. The slurry was left to stir for 24 hours, after which any remaining water was removed using a rotary evaporator, the catalyst was then put in an oven and left to dry. Once the catalyst was dry it was ground and graded by particle size, retaining the fraction between 250 and 500μm to be calcined. The calcined catalyst was then used for reaction testing.

3.3 OTHER CATALYSTS USED FOR THIS PROJECT

3.3.1 The ICI Synetix supplied 1% Pd/C catalyst

This catalyst was prepared by ICI Synetix. In summary, it was prepared by a incipient wetness technique with $Pd/(NO_3)_2$ and a charcoal support. The support material is Norit RX3 with a pore volume of 0.63 m/g. The support was supplied as extrude. The metal loading, as determined by atomic absorption was 1.00%. This catalyst was used for the bulk of the initial studies into the selective hydrogenation of 2-butyne-1,4-diol in this project. Before use the catalyst was ground and graded by particle size; retaining the fraction between 250 and 500μm.

3.3.2 The Copper catalyst used in this project

This catalyst was prepared at Glasgow University by D. Anderson, and extensive information on its preparation, characterisation and catalytic activity is available [1]. In summary, it was prepared by a wet impregnation technique with $Cu(NO_3)_2.2.4H_2O$ and Cab-O-Sil. The metal loading, as determined by atomic absorption was 9.1%. Before use the catalyst was ground and graded by particle size; retaining the fraction between 250 and 500μm.

3.4 CATALYST CHARACTERISATION

3.4.1 Surface area determination

Approximately 0.05g of each of the palladium catalysts was weighed into a surface area sample tube. These samples were dried for three days to remove any residual moisture. The surface area determination was conducted on a Micrometrics surface area analyser, using N_2 as the adsorbate. Data for BET total surface area, total pore volume and pore size distribution was obtained.

3.4.2 Transmission electron microscopy (TEM)

TEM is a commonly applied form of electron microscopy for the studying of supported metal catalysts. It is generally possible to detect and resolve supported metal particles provided that there is sufficient contrast between the metal and support material. This contrast is a function of the extent to which the electrons are scattered by the different materials, which is affected by such factors as the identity of the species in question, their crystallinity and the sample thickness. On highly dispersed supported oxide catalysts, sufficient contrast between the metal and the support may be a problem.

"Bright-field" techniques are most regularly used in transmission electron spectroscopy. In 'bright-field' techniques the image is obtained from electrons in the optic axis passing directly through the sample. It is also possible to focus the electrons that are scattered or diffracted upon passing through the sample, thereby producing a 'dark-field' image [2]. The micrographs that were obtained during the course of this study were mostly bright-field images.

Samples of the palladium catalysts were prepared by grinding 0.15g of catalyst into a fine powder, which was then suspended in distilled water and ultrasonically dispersed for 20 minutes. A drop of the fine suspension was then placed on a 300square mesh Cu carbon coated grid. The grid was then put in an oven at 40^0C to dry overnight. After drying the sample was ready for analysis, the measurements were made on a 002B High Resolution Transmission Electron Microscope, supplied by Topcon for the 1% Pd/C catalyst and a Philips 1200 electron microscope for the 1% Pd/Al_2O_3 catalysts.

Energy dispersive x-ray spectroscopy (EDX) was considered to confirm the identity of the palladium particles for 1% Pd/C catalyst. For selected samples particle size distributions were determined, by measuring the diameters of the particles on a selection of negatives at different magnifications. The micrographs were measured in this way to ensure a representative sample of the catalyst surface.

3.4.3 Chemisorption

Knowledge of the catalyst surface is important to achieve a greater understanding of any support metal catalyst. Conducting chemisorption experiments is one way of gaining an increased understanding of the catalyst surface. It was necessary to do chemisorption experiments on the palladium catalysts that were used in this study, to determine the fraction of the total metal atoms that are exposed at the surface of the catalyst, to help increase the understanding of how the catalysts perform under reaction conditions. Carbon monoxide was used to determine the fraction of the total number of metal atoms that are exposed at the surface of the catalyst. Once the number of surface metal atoms had been determined the % dispersion of the catalyst could be determined using the equation below.

Equation 3.4.3

$$\% \text{ Dispersion} = \frac{\text{No. Surface Metal Atoms}}{\text{Total No. Metal Atoms Per Sample}} \times 100\%$$

A quantity of a gas will be chemisorbed at the surface forming a fraction of a monolayer, when a known volume of an adsorbate gas is pulsed over a freshly reduced catalyst. If pulsing is continued of the known amount of adsorbate gas then more gas will be adsorbed until a monolayer is formed, once the monolayer has been formed then no further gas will react at the surface. Flow chemisorption only determines the amount of material permanently retained at the adsorption temperature. Pulsed chemisorption assumes that there is little or no contribution from the support to the observed chemisorption process. This allows a direct stoichiometry between the number of exposed metal atoms and the gas molecules to be applied. Carbon monoxide adsorption experiments were performed on all the palladium catalysts used in this study, to determine the degree of metal atom dispersion over the support materials, and to determine the average metal crystallite sizes.

The pulse-flow gas chemisorption apparatus shown in Figure 3.4.3.2 was used to conduct the chemisorption experiments. The apparatus consisted of a flow line, vacuum section and a known volume sample loop. By combining both a rotary pump and a mercury diffusion pump, a vacuum of 10^{-4} Torr or better was achieved, with the vacuum being measured directly using a Pirani Gauge. To remove the possibility of mercury vapour poisoning the catalysts and to protect the oil pump from condensable gases, cold traps containing liquid nitrogen were used.

A bulb attached to the line via a manifold was used to store the carbon monoxide. The carbon monoxide could be admitted into the known volume sample loop and the pressure measured using a pressure transducer, by isolating the manifold form the vacuum section. This known amount of gas (4.70 cm^3, 14 mbar) was then injected into a helium carrier gas flow over the reduced catalyst. Direct monitoring of any changes in the gas composition was achieved by using a TCD that was placed directly in the gas flow.

Approximately 0.3000g of catalyst were reduced *in-situ* in a flow of 6% H_2/N_2 using the standard programmed reduction, with the same reduction profile as detailed in section 3.5.1, for the purposes of the chemisorption experiments. When the catalyst reduction was complete, the 6% H_2/N_2 was switched to helium and the catalyst was allowed to cool to ambient temperature. A deoxygenating catalyst, 5% Pd/WO_3 was used to purify the gas flows before they reached the catalyst, with the gas flows also being dried by passing through a molecular sieve trap before they reached the catalyst.

Calibration of the system was necessary before the adsorption experiments could be performed. To calibrate, standard pulses of the adsorbate were pulsed into the helium flow, they were carried by the helium to the output from which was fed a TCD connected to a Hewlett Packard 3395 Integrator. These pulses by-passed the catalyst sitting in the reactor and produced distinct peaks on the integrator. After three identical pulses were achieved on the integrator, the system was ready to conduct a chemisorption experiment on. Pulses of known size were directed over the catalyst, the uptake of the pulsed gas could

be measured as the difference in the eluted peaks and the calibration peaks. The pulsing procedure was continued until peaks of equal area were obtained, this would indicated the formation of a monolayer (as the available metal sites at this point had no more capacity to adsorb carbon monoxide). A typical chemisorption trace is detailed in Figure 3.4.3.1

Figure 3.4.3.1 Typical chemisorption trace

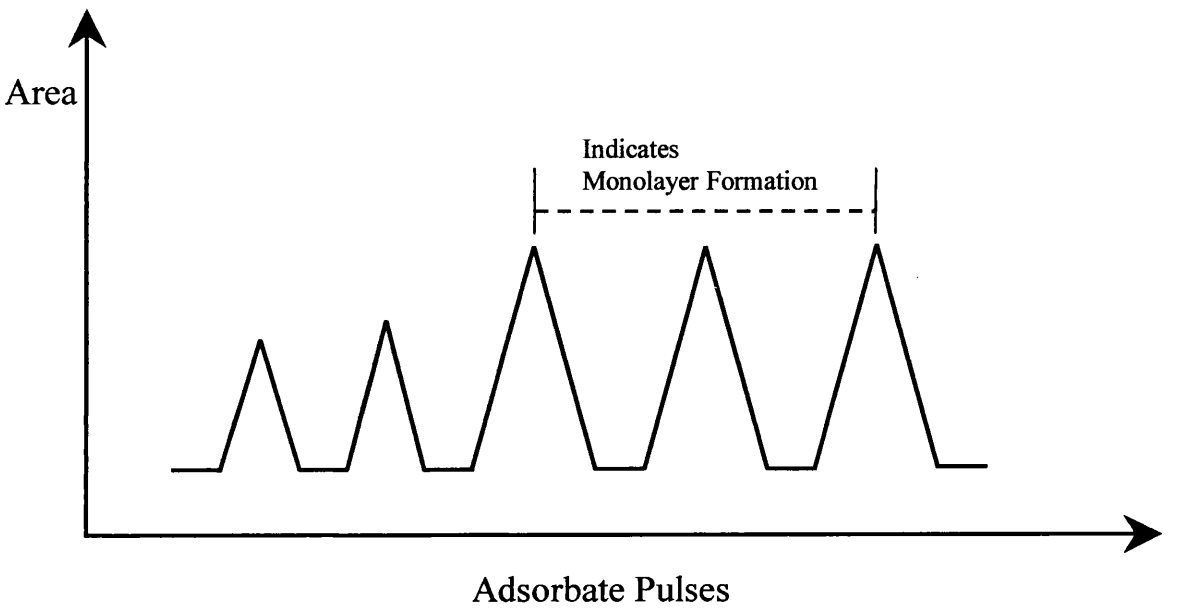
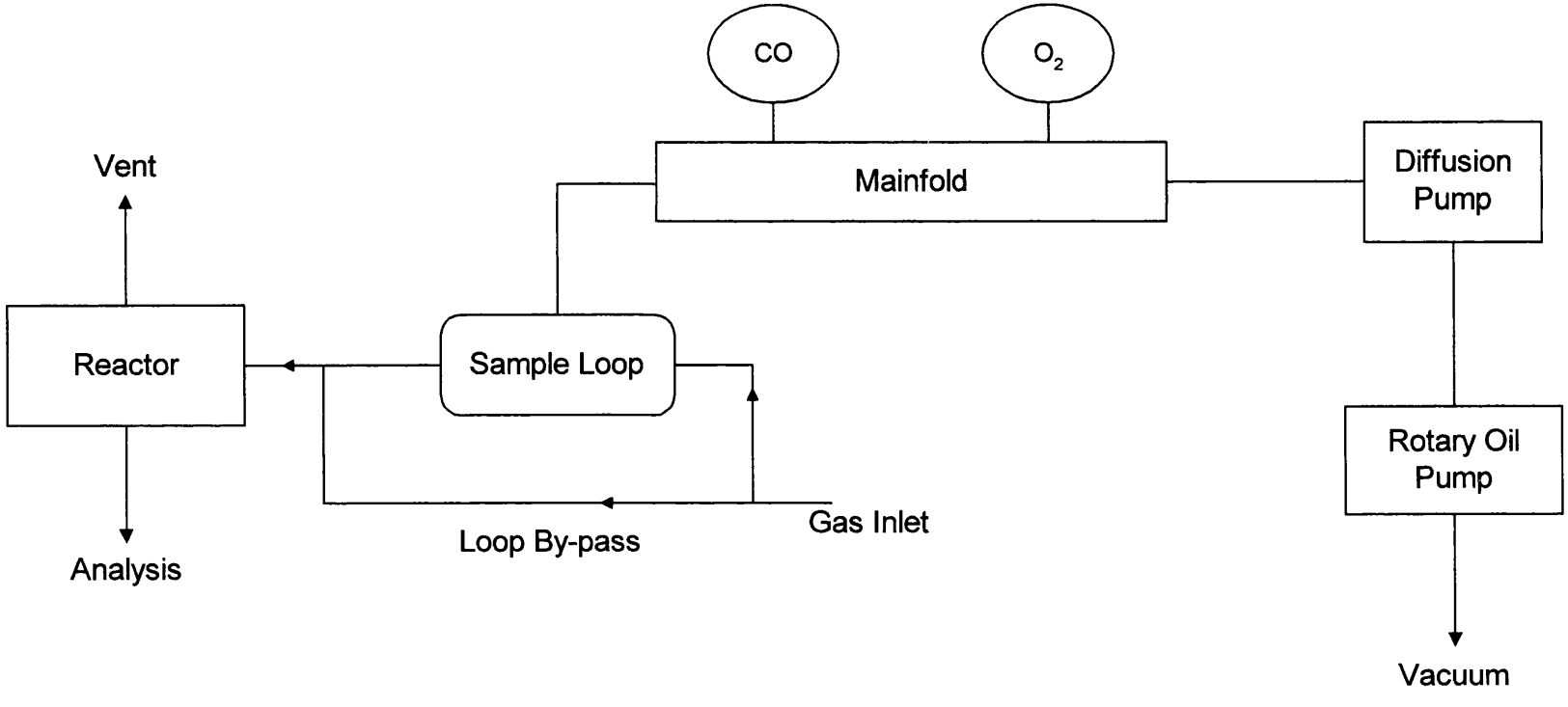


Figure 3.4.3.2 Chemisorption apparatus



3.5 AMBIENT PRESSURE REACTIONS

The liquid-phase ambient pressure apparatus detailed in Figure 3.5.1 was designed so that three reactions could be carried out simultaneously in three ambient pressure reactors. The ambient pressure apparatus allows any two out of four gases (*i.e.* H_2, 6% H_2/N_2, He or D_2) to be delivered to the ambient pressure reaction vessels at the same time at varying flows. This set-up enables duplicate experiments, or a series of runs to be conducted quickly and efficiently. The ambient pressure reaction vessels allow for the catalyst to be reduced *in-situ*.

3.5.1 Temperature programmed reduction procedure for palladium catalysts in the ambient reaction vessel

0.2500g of the catalyst of the desired palladium catalyst was introduced into the reaction vessel, and was reduced in a stream of 6% H_2/N_2 (at a flow rate of 45ml/minute), the reactor vessel was in the 'inverted' *i.e.* the reduction position during the reduction detailed on Figure 3.5.2. Using a temperature programmer supplied by Eurotherm, and a heating jacket attached to the reaction vessel, the catalyst was heated to 200^0C. A ramp rate of 3^0C/minute was used for the reduction. The catalyst was held at 200^0C for a further hour, after which it was allowed to cool for 45 minutes in a stream of helium (at a flow rate of 200ml/minute) to ambient temperature.

3.5.2 Non-programmed reduction procedure for palladium catalysts in the ambient reaction vessel

Some of the liquid-phase ambient pressure experiments were conducted without a programmed reduction. For these experiments 0.2500g of a palladium was introduced into the reaction vessel when in was in the reaction position detailed in Figure 3.5.2 (with the condenser already attached). 40ml

of propan-2-ol was then added into the reaction vessel, and a flow rate of 200ml/minute of H_2 was then sparged through the propan-2-ol and catalyst slurry. The slurry is set to stir at a relative stirrer speed of 7, and then left for 30 minutes to reduce the catalyst fully. The heating element in the stirrer/hotplate was turned on 20 minutes into the reduction procedure, to ensure the oil bath was at the correct temperature for the reaction when the reduction was finished.

3.5.3 Temperature programmed reduction procedure for copper catalysts in the ambient reaction vessel

0.8000g of the catalyst of the desired copper catalyst was introduced into the reaction vessel, and was reduced in a stream of 6% H_2/N_2 (at a flow rate of 150ml/minute), the reactor vessel was in the 'inverted' *i.e.* the reduction position during the reduction. Using a temperature programmer supplied by Eurotherm, and a heating jacket attached to the reaction vessel, the catalyst was heated to 300^0C. A ramp rate of 3^0C/minute was used for the reduction. The catalyst was held at 300^0C for a further hour, after which it was allowed to cool for 45 minutes in a stream of helium (at a flow rate of 200ml/minute) to ambient temperature.

3.5.4 Reaction procedure for the ambient reaction vessel that used a programmed reduction with a palladium catalyst

After the reduction was complete the reactor vessel was turned to the reaction position. The degassed reactant solution of 2-butyne-1,4-diol in propan-2-ol (80ml of 0.233M 2-butyne-1,4-diol in propan-2-ol) was injected, using a glass syringe, into the reactor vessel. Once the introduction of the reactant solution was complete, the condenser was fitted to the vessel. The vessel was then lowered into oil bath (set at 65^0C with a relative stirrer speed of 7) that was heated and stirred by the IKA RCT Basic oil bath/magnetic stirrer. A H_2 flow

rate of 200ml/minute (selected using the Platon flowmeter) was then introduced to the reaction mixture through the gas sparges (see Figure 3.5.2). 0.4ml samples were taken periodically from the reactor vessel during the course of the reaction and filtered, and then analysed using the Shimadzu GC-14A gas chromatograph.

3.5.5 Reaction procedure for the ambient reaction vessel that used a non-programmed reduction with a palladium catalyst

Once the reduction was complete, the degassed reactant solution of 2-butyne-1,4-diol in propan-2-ol (40ml of 40g 2-butyne-1,4-diol per litre of propan-2-ol) was introduced into the reaction vessel, and the reaction commenced. 0.4ml samples were taken periodically from the reactor vessel during the course of the reaction and filtered, and then analysed using the Shimadzu GC-14A gas chromatograph.

3.5.6 Reaction procedure for the ambient reaction vessel that used a programmed reduction with a copper catalyst

After the reduction was complete the reactor vessel was turned to the reaction position (see figure 6). The degassed reactant solution of 2-butyne-1,4-diol in propan-2-ol (80ml of 0.233M 2-butyne-1,4-diol in propan-2-ol) was injected, using a glass syringe, into the reactor vessel. Once the introduction of the reactant solution was complete, the condenser was fitted to the vessel. The vessel was then lowered into oil bath (set at 65^0C with a relative stirrer speed of 7) that was heated and stirred by the IKA RCT Basic oil bath/magnetic stirrer. A H_2 flow rate of 200ml/minute (selected using the Platon flowmeter) was then introduced to the reaction mixture through the gas sparges. 0.4ml samples were taken periodically from the reactor vessel during the course of the reaction, and analysed using the Shimadzu GC-14A gas chromatograph.

Figure 3.5.1 Ambient pressure apparatus

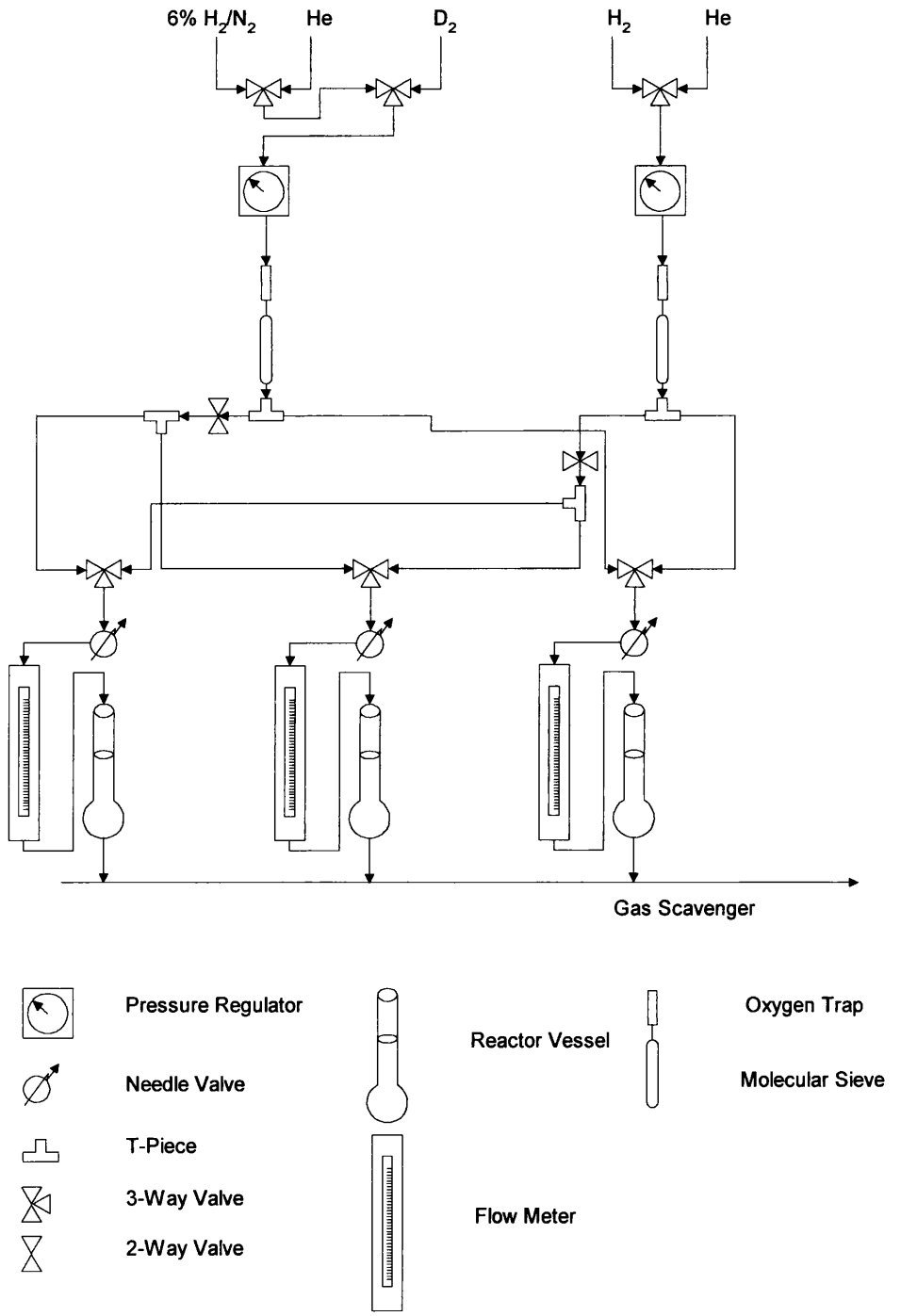
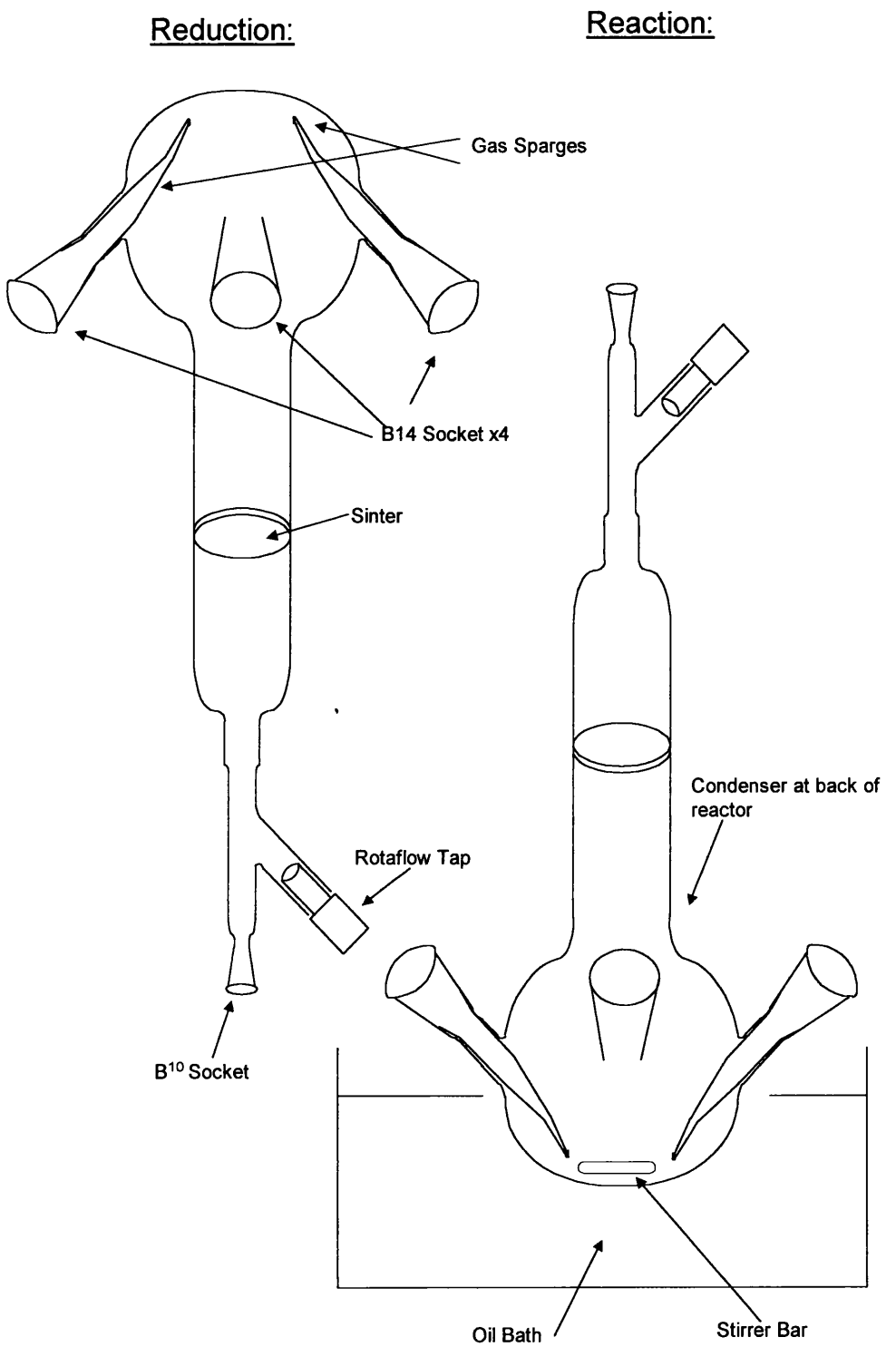


Figure 3.5.2 Ambient pressure reactor



3.6 ELEVATED PRESURE REACTIONS

The elevated pressure reactions were carried out using a elevated pressure reactor supplied by Buchi, detailed in Figure 3.6.2, with the reactions that used *ex-situ* reduction using the ex-situ reduction vessel detailed in Figure 3.6.1 All of the reactions detailed in this study were conducted at 2bar gauge.

3.6.1 *Ex-situ* programmed reduction procedure for elevated pressure reactor for the 1% Pd/C catalyst

1.2500g of the 1% Pd/C catalyst was introduced into the *ex-situ* reduction vessel. The scavenger tap on the elevated pressure reactor is opened, and a tube is connected between the elevated pressure reactor and the *ex-situ* reduction vessel. This tube enables the *ex-situ* reduction vessel to use the scavenger from the elevated pressure reactor, and once reduction is finished it allows the transport of the catalyst to the elevated pressure reactor without contact with the laboratory atmosphere. The catalyst was reduced in a stream of 6% H_2/N_2, at a flow rate of 60ml/minute. Using a temperature programmer supplied by Eurotherm, and a furnace supplied by Watlo that the *ex-situ* reduction vessel sat in, the catalyst was heated to 200^0C. A ramp rate of 3^0C/minute was used for the reduction. The catalyst was held at 200^0C for a further hour, after which it was allowed to cool for 45 minutes in a stream of helium (at a flow rate of 200ml/minute) to ambient temperature.

3.6.2 Non-programmed reduction procedure for 1% Pd/C catalysts in the elevated pressure reaction vessel

Some of the liquid-phase elevated pressure experiments were conducted without a programmed reduction. For these experiments 1.2500g of the 1% Pd/C catalyst was introduced into the elevated pressure reaction vessel. 300mls of propan-2-ol was then introduced in the elevated pressure reaction

vessel. The scavenger tap on the elevated pressure reaction vessel was opened, to reduce the catalyst H_2 gas was bubbled through the propan-2-ol/catalyst slurry, at a flow rate of 100ml/minute. A stirrer speed of 300rpm was used to agitate the propan-2-ol/catalyst slurry to ensure the complete reduction of the catalyst. The catalyst was allowed to reduce for 1 hour, the oil bath heater system was then turned on to allow the reaction vessel to reach reaction temperature.

3.6.3 *Ex-situ* programmed reduction procedure for elevated pressure reactor for the 9.1% $Cu/Cu(NO_3)_2$ on silica catalyst

4.0000g of the 9.1% $Cu/Cu(NO_3)_2$ on silica catalyst was introduced into the *ex-situ* reduction vessel. The scavenger tap on the elevated pressure reactor is opened, and a tube is connected between the elevated pressure reactor and the *ex-situ* reduction vessel. This tube enables the *ex-situ* reduction vessel to use the scavenger from the elevated pressure reactor, and once reduction is finished it allows the transport of the catalyst to the elevated pressure reactor without contact with the laboratory atmosphere. The catalyst was reduced in a stream of 6% H_2/N_2, at a flow rate of 300ml/minute. Using a temperature programmer supplied by Eurotherm, and a furnace supplied by Watlo that the *ex-situ* reduction vessel sat in, the catalyst was heated to 300^0C. A ramp rate of 3^0C/minute was used for the reduction. The catalyst was held at 200^0C for a further hour, after which it was allowed to cool for 45 minutes in a stream of helium (at a flow rate of 200ml/minute) to ambient temperature.

3.6.4 Reaction procedure for the elevated pressure reactions that used *ex-situ* programmed reduction with the 1% Pd/C catalyst

After the reduction was complete the reduction vessel was sealed from the gas supply, to enable the catalyst to be tipped into the elevated pressure reactor using the length of PTFE tubing that connected the reduction vessel and elevated pressure reactor during reduction. When catalyst was introduced into the elevated pressure reactor it already contained 300mls of degassed propan-2-ol (which had been heated to 65^0C for the reaction using the oil heater system). The degassed reactant solution of 2-butyne-1,4-diol in propan-2-ol (8.000g 2-butyne-1,4-diol dissolved in 100mls of propan-2-ol) was injected using a glass syringe into the reactant injection port on the elevated pressure reactor, and the scavenger tap was closed. Once the catalyst and reagent solution had been introduced, the reaction slurry went through a degassing procedure to purge any unwanted air from the reaction vessel. After the purging was finished the stirrer in the elevated pressure reaction vessel was set to 800rpm. A H_2 pressure of 2bar gauge, was used during the course of the reaction. Samples were periodically taken form the elevated pressure reactor by slowing the stirrer and taking the sample from the gas/sample three-way tap. The sample was then filtered and analysed using the Shimadzu GC-14A gas chromatograph.

3.6.5 Reaction procedure for the elevated pressure reactions that employ non-programmed reduction of 1% Pd/C catalyst.

Once the reduction was finished, the degassed reactant solution of 2-butyne-1,4-diol in propan-2-ol (8.000g 2-butyne-1,4-diol dissolved in 100mls of propan-2-ol) was injected using a glass syringe into the reactant injection port on the elevated pressure reactor, and the scavenger tap was closed. Once the catalyst and reagent solution had been introduced, the reaction slurry went through a degassing procedure to purge any unwanted air from the reaction vessel. After the purging was finished the stirrer in the elevated pressure reaction vessel was set to 800rpm. A H_2 pressure of 2bar gauge, was used

during the course of the reaction. Samples were periodically taken form the elevated pressure reactor by slowing the stirrer and taking the sample from the gas/sample three-way tap. The sample was then filtered and analysed using the Shimadzu GC-14A gas chromatograph.

3.6.6 Reaction procedure for the elevated pressure reactions that used *ex-situ* programmed reduction with the 9.1% $Cu/Cu(NO_3)_2$ on silica catalyst

After the reduction was complete the reduction vessel was sealed from the gas supply, to enable the catalyst to be tipped into the elevated pressure reactor using a length of PTFE tubing that connected the reduction vessel and elevated pressure reactor during reduction. When catalyst was introduced into the elevated pressure reactor it already contained 300mls of degassed propan-2-ol, which had been heated to 65^0C for the reaction using the oil heater system. The degassed reactant solution of 2-butyne-1,4-diol in propan-2-ol (8.000g 2-butyne-1,4-diol dissolved in 100mls of propan-2-ol) was injected using a glass syringe into the reactant injection port on the elevated pressure reactor, and the scavenger tap was closed. Once the catalyst and reagent solution had been introduced, the reaction slurry went through a degassing procedure to purge any unwanted air from the reaction vessel. After the purging was finished the stirrer in the elevated pressure reaction vessel was set to 800rpm. A H_2 pressure of 2bar gauge, was used during the course of the reaction. Samples were periodically taken form the elevated pressure reactor by slowing the stirrer and taking the sample from the gas/sample three-way tap. The sample was then filtered and analysed using the Shimadzu GC-14A gas chromatograph.

Figure 3.6.1 *Ex-situ* reduction apparatus for catalysts employing the elevated pressure reaction vessel

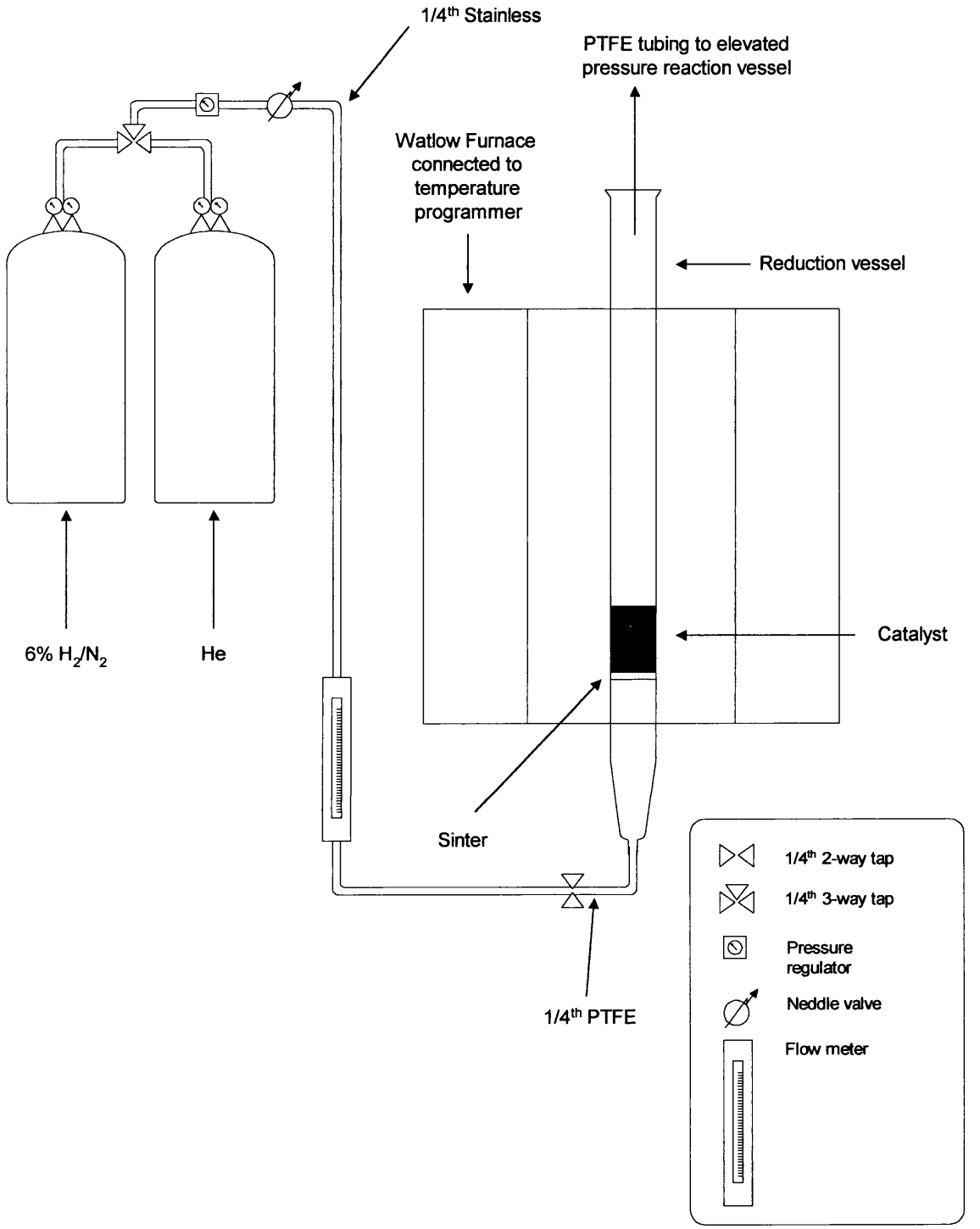
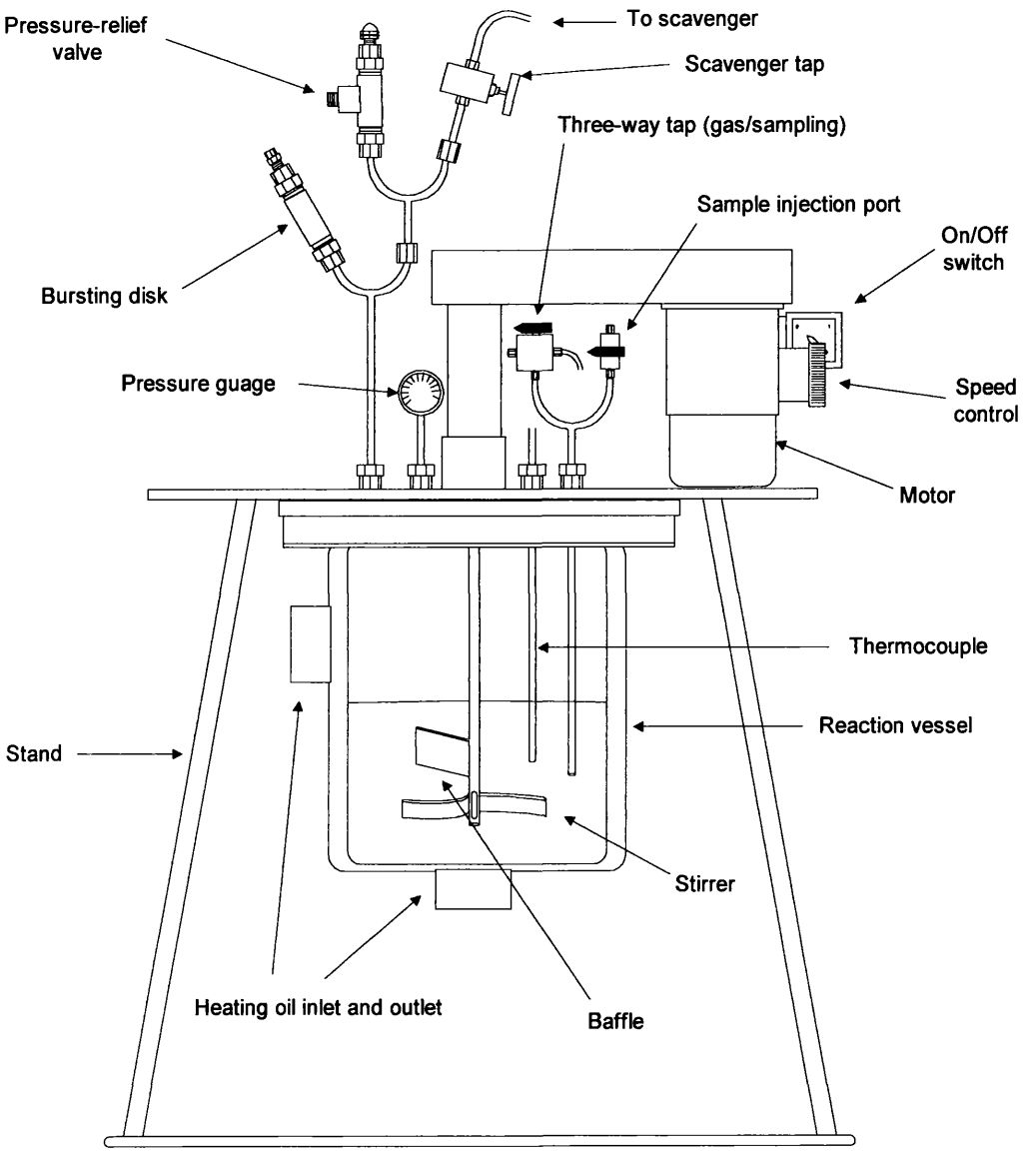


Figure 3.6.2 Buchi liquid phase hydrogenator



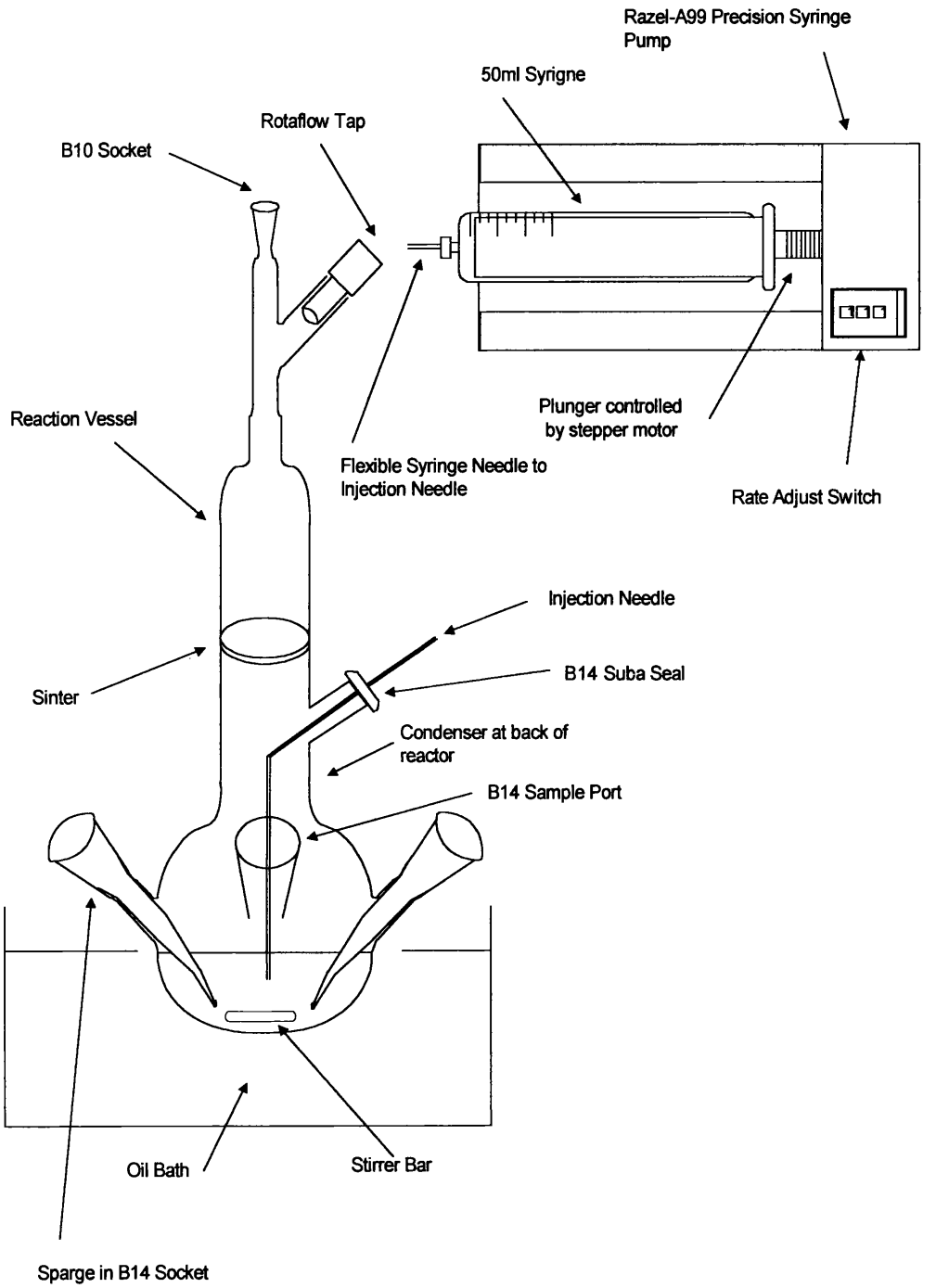
3.7 REACTION PROCEDURE FOR CONTINUOUS ADDITION REACTIONS

For continuous addition reactions an ambient pressure reactor was modified so that it had another B14 socket to allow for the introduction of material into the vessel during reaction through the injection needle, see Figure 3.7. Two solutions of 2-butyne-1,4-diol were prepared with concentrations of 1.05M and 0.233M in propan-2-ol. After reduction of the 1% Pd/C catalyst, it was immersed in 80mls of the 0.233M 2-butyne-1,4-diol solution (the procedure being the same for the reduction as detailed in Section 3.5.1). Instead of injecting all of the 1.05M 2-butyne-1,4-diol solution into the reactor at the beginning of the reaction, 45mls of this solution was injected into the reactor over a period of approximately ten hours. This was achieved by charging 45mls of the 1.05M 2-butyne-1,4-diol solution into a 50ml syringe, which was then placed on the precision syringe pump (detailed below). 0.4ml samples were taken via a suba seal periodically from the reactor vessel during the course of the reaction, and analysed using the Shimadzu GC-14A gas chromatograph.

3.7.1 The Razel Model A-99 Syringe Pump

The Razel Model A-99 syringe pump was used for accurate injection of the 1.05M 2-butyne-1,4-diol into the reactor during the continuous addition reactions. The Razel Model A-99 pump was designed to introduce a fluid at a reproducible flow rate from a syringe. Pulses produced by a stepper motor are used to control the feed rate from the pump, it has a pressure limit of 270mm/Hg for a 50ml syringe. The pump has 99 selectable flow rates, which are readily changeable by a single switch, it contains a shut-off switch for when the syringe becomes empty, changing the size of syringe allows different feed rates of solution to be achieved. For the purposes of the continuous addition series of experiments a pumping speed of 1.444ml/hr for a 50ml syringe was selected.

Figure 3.7 Continuous addition apparatus



3.8 PROCEDURE FOR THE ISOLATION OF ISO-PROPOXYTETRAHYDROFURAN THROUGH MICRO-DISTILLATION

Iso-propoxytetrahydrofuran is a major product that is produced during the reactions detailed in this thesis that employ the palladium catalysts. It was an originally unexpected product that is discussed in more detail in Section 5.11 and Chapter 6. To isolate and quantify iso-propoxytetrahydrofuran micro-distillation apparatus was used, detailed in Figure 3.8.

The reaction procedure involved the use of the elevated pressure reaction vessel for a couple of reasons; the rate of hydrogenation is quicker in the elevated pressure reaction vessel and the large volume of the elevated pressure reaction vessel allowed for reactions that could produce relatively large quantities of iso-propoxytetrahydrofuran. The reaction procedure itself was the same as the reduction procedure in Section 3.6.1 and the reaction procedure in section 3.6.4 for elevated pressure reactions, with one exception. The concentration of 2-butyne-1,4-diol that was introduced into the reaction vessel was 2.33M, ten times more than in a standard reaction. This increased concentration of 2-butyne-1,4-diol was used in order to increase the yield of iso-propoxytetrahydrofuran that was produced in the reaction vessel. The reaction was allowed to continue overnight until there was no further reaction. 0.4ml samples where taken form the reaction vessel periodically to check the progress of the reaction, the catalyst was filtered off and the samples were analysed by GC.

Once the reaction was complete the resultant reactant solution was filtered to remove the catalyst and transferred into a labelled 500ml volumetric flask. This solution was used in several batches to try to isolate the iso-propoxytetrahydrofuran. For the micro-distillation 30mls of the solution was introduced with boiling chips into the sample flask with the stirrer bar (the boiling chips being present to prevent bumping). The sample solution was heated from between 40-90°C. Within this temperature range a number of

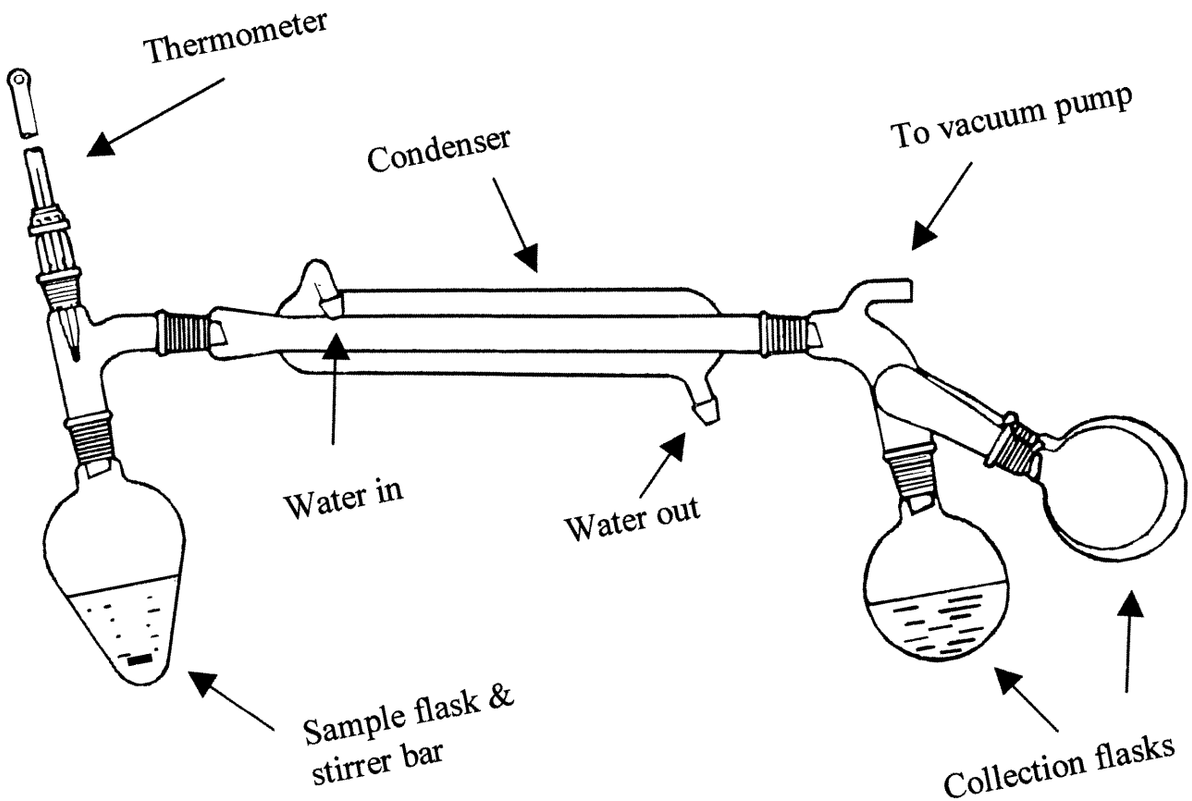
different fractions were taken off and tested using GC analysis for the concentrations of their constituent components.

3.8.1 Using ^{1}H and ^{2}D NMR spectroscopy for the identification of iso-propoxytetrahydrofuran

All the proton NMR experiments were conducted using a DPX 400MHz NMR spectrometer. $CDCl_3$ was used to dilute the samples (1 part sample:4 parts $CDCl_3$) 1ml of undiluted sample was required for this, samples were then place in a nmr tube (5mm in diameter) and inserted into the spectrometer. Due to the dominant solvent feature within each sample (each sample being ~90% solvent before dilution) all spectra had to be expanded so that the reaction products were visible.

The ^{2}D experiments were conducted on a WP 200MHz NMR spectrometer, all the samples were run without dilution with $CDCl_3$. 4ml of each sample was required for each 10mm diameter NMR tube, the samples were than placed in the spectrometer and run.

Figure 3.8 Micro-distillation apparatus



3.9 ANALYSIS OF SAMPLES

Gas chromatograph-mass spectrometry (GC-MS) was used for the identification of the reaction products obtained, by comparison of their retention times through the column against known standards, and in some cases through a combination of NMR techniques and GC-MS. For everyday quantitative analysis of the reaction products gas chromatography was employed.

A Hewlett Packard 5890 Series II gas chromatograph interfaced with a Hewlett Packard 5971 Series mass selective detector was used for primary identification of the species observed in the reactions. The Hewlett Packard 5890 Series GC-MS was controlled through an interface to a Vectra QS 165 computer. For the GC-MS analysis, a SGE BP20 0.25 capillary was used for the separation of the reaction products, it was 30m long, 0.25mm ID, 0.33mm OD and had a polyethylene glycol stationary phase.

Gas chromatography was used for the verification of the identities' of the species present during reaction testing, by comparing the retention time in the column with those of known standards. The gas chromatograph that was used for this study was a Shimadzu GC-14A equipped with a flame ionisation detector (FID). An integrator supplied by Hewlett Packard allowed direct examination of chromatographic data. The capillary column that was used with the Shimadzu GC-14A was the same as the one supplied by SGE, detailed above. The sensitivity of the GC was calibrated with a standard solution to ensure precision of analysis, before analysis of the reaction samples.

3.9.1 Gas chromatography operating conditions

For both the GC and GC-MS analyses the oven temperature of the gas chromatograph was controlled in 3 ramps, 80-120^{0}C, 120-195^{0}C and 190-220^{0}C. The flow rate through the capillary column was 2ml/minute, the split flow rate was 50ml/minute, (helium was used as the carrier gas) this gave a split ratio of 1:25, the make-up gas flow rate was 45ml/minute of helium. The FID required of 300ml/minute flow of oxygen and 30ml/minute of hydrogen. The detector temperature was 240^{0}C, the injector temperature was 240^{0}C.

3.10 MATERIALS

Chemicals were purchased from Aldrich, with the purities shown by Table 3.10.

Table 3.10: Materials used for project

Chemical	Purity (%)
2-butyne-1,4-diol	99
Cis-2-butene-1,4-diol	95
Butane-1,4-diol	99 +
Crotyl Alcohol	97
3-buten-1-ol	99
2-butyne-1ol	98
3-butyne-1-ol	98 +
Propan-2-ol	99.95
Butan-1-ol	99.95

Chemicals were used as supplied without further purification, reaction mixtures for both the ambient and elevated pressure reactors were degassed with helium prior to use.

Gases supplied by BOC were H_2, He and 10% H_2/N_2 mixture. These were purified further before use, using deoxygenating catalysts and molecular sieves installed in the reaction lines.

Chapter Four

TREATMENT OF RESULTS

4.0 TREATMENT OF RESULTS

The reaction testing results are generally plotted as the number of moles of the reactant consumed/product formed versus the reaction time. The number of moles of 2-butyne-1,4-diol, *cis*-2-butene-1,4-diol, butane-1,4-diol, butanol, *cis* and *trans*-crotyl alcohol, 3-buten-1-ol and iso-propoxytetrahydrofuran for each sample were calculated from calibration curves for each of the species, that were produced using known concentration standards.

Once the quantities of each of the aforementioned species had been determined, the results of the reaction testing have been represented using the following definitions:-

Equation 4.1

$$\text{Selectivity} = \frac{\text{No. moles } cis-2-\text{butene}-1,4-\text{diol formed}}{\text{No. moles of } 2-\text{butyne}-1,4-\text{diol consumed}} \text{ x } 100\%$$

Equation 4.2

$$\text{Conversion} = \frac{\text{No. moles } 2-\text{butyne}-1,4-\text{diol reacted}}{\text{No. moles of } 2-\text{butyne}-1,4-\text{diol present initially}} \text{ x } 100\%$$

Reaction rates that have been listed in the comparison tables have been normalised to 1g of catalyst. They are expressed as moles/litre/s/g catalyst to allow for comparisons of catalyst activity for the different reaction regimes that are reported in this study. The values expressed were calculated using linear lines of best fit derived via a computer program (Excel).

The error bars that are displayed in the reaction profiles were determined by analysing a 0.233 molar 2-butyne-1,4-diol solution 200 times with the Shimadzu G.C. 14a, and multiplying the standard deviation by 2 from these analyses, to obtain an error of 5.996% in the concentration of the species present for each G.C. analysis. The selectivities and conversions for the reactions detailed in this study are quoted to two decimal places, the concentrations of the reaction species are quoted to four decimal places in the summary tables.

The turnover frequency has been defined as the number of moles reacting per litre per second, per active site on the catalyst, assuming that every surface palladium atom behaves as an active site.

Chapter Five

RESULTS AND DISCUSSION PART (I)

5.1 CATALYST CHARACTERISATION

5.1.1 Surface area measurements (BET)

The BET surface areas and porosities for the catalyst supports and the calcined catalysts are given in Table 5.1.1 for the 1% palladium catalysts. Characterisation for the 9.1% Cu/SiO_2 catalyst is detailed in David Anderson's PhD thesis [1]. Table 5.1.1 is a summary table of the surface area results for the 1% supported palladium catalysts that were employed in this study.

Table 5.1.1: Summary of surface area results for 1% supported palladium catalysts

	Catalyst or Support	N_2 Surface Area (m^2/g)	Total Pore Volume (cm^3/g)	Average Pore Diameter (nm)
Carbon support	Norit RX3	1199.50	0.63	2.30
	1% Pd/C	1104.31	0.63	2.30
Alumina support	Aluminium Oxid C	100.31	-	-
	1% Pd/Al_2O_3 ($PdCl_2$)	91.57	0.44	19.05
	1% Pd/Al_2O_3 ($Pd(NO_3)_2$)	96.35	0.56	17.12

The results show that all three of the 1% palladium catalysts used in this study have surface areas in excess of 91 m^2/g. It is apparent from the above table that the two Aluminium Oxid C supported catalysts have significantly lower surface areas than the 1% Pd/C catalyst (supplied by Synetix) which employed Norit RX3 as the support material.

These significantly different surface areas (in combination with other catalyst morpholigical factors) may lead to different chemistry being observed in the results reported in this study.

5.1.2 Chemisorption

Section 3.4.3 gives a brief description of chemisorption, and how, using Equation 3.4.3, average % dispersion values can be obtained from CO chemisorption experiments (assuming a 2:1 CO:Pd ratio with the CO occupying mostly bridged sites [2]). To obtain particle sizes from dispersion data, assumptions must be made concerning particle shape, that is it was assumed that the supported metal particles were spheres of equal diameter (d). The dispersion of a metal (D) varies as the reciprocal of the average particle size, and as such the larger the value of D the smaller the average particle size [3], equation 5.1.2:-

Equation 5.1.2:

$$\% \text{ Dispersion} = \frac{A \times 6}{\rho \times S_a \times N_a \times d} \times 100\%$$

where A = atomic weight

ρ = density of metal

S_a = average surface area occupied by 1 active atom

N_a = Avogadro's number

d = average particle diameter

This equation is identical to that used by Smith, Thrower and Vannice [4]. It is equally valid for cubic particles with edges of length d. Hence for palladium, A = 106.42 a.m.u., $\rho = 12.02 \times 10^{-21}$ g/nm^3, Sa = 0.0806 nm^2 and d = 109/D nm. Table 5.2.1 is a summary table for the chemisorption experiments conducted on the three 1% palladium catalysts. It shows that the dispersion for the 1% Pd/C catalyst was only 9.56%, while the dispersion for the 1% Pd/Al_2O_3 (nitrate precursor) and the 1% Pd/Al_2O_3 (chloride precursor) were 94.41% and 70.01% respectively. As with the surface area results detailed above, this difference in the dispersions for the different catalysts may lead to different reaction chemistry being observed.

Table 5.1.2 Summary table for dispersion data for 1% palladium catalysts

Catalyst	Uptake CO Mole/g catalyst	Pd surface/g catalyst	Dispersion	Ave. particle size by chemisorption	Ave. particle size by E.M.
1% Pd/C	4.49×10^{-6}	5.41×10^{18}	9.56%	11.40 nm	12.41
1% Pd/Al_2O_3 (nitrate precursor)	4.44×10^{-5}	5.34×10^{19}	94.41%	1.15 nm	-
1% Pd/Al_2O_3 (chloride precursor)	3.29×10^{-5}	3.29×10^{19}	70.01%	1.56 nm	-

The 1% Pd/C catalyst was examined using the Topcon 002B High Resolution Transmission Electron Microscope, the 1% Pd/Al_2O_3 catalysts were examined employing a Philips 1200 electron microscope. The Philips 1200 was unable to produced micrographs of sufficient resolution to allow for the determination of the sizes of the metal particles using visual inspection of the micrographs.

5.1.1 SUMMARY FOR SECTION 5.1

- The minimum N_2 surface area for the 1% palladium catalysts was 91.57 m^2/g (for the chloride precursor catalyst), the 1% Pd/C catalyst had a N_2 surface area of 1104.31 m^2/g.

- The dispersion for the 1% Pd/Al_2O_3 catalysts were considerable higher than that for the 1% Pd/C catalyst.

- The different catalyst characterisation for the three 1% palladium catalysts may lead to different reaction chemistry being observed during the reaction testing.

5.2 AMBIENT AND ELEVATED PRESSURE REACTIONS

This section summarises reactions that were conducted at ambient and elevated pressure. They were conducted primarily to investigate the liquid phase selective hydrogenation of 2-butyne-1,4-diol to *cis*-2-butene-1,4-diol, but also the hydrogenation of *cis*-2-butene-1,4-diol to try and further understand the overall reaction scheme. Evaluation of the reaction chemistry in different reactors and at different pressure provides a more comprehensive assessment of the chemical pathways accessible within this reaction system. This section can be further divided into three parts, i) ambient pressure reactions (Figures 5.2.1, 5.2.2 and 5.2.3), ii) elevated pressure reactions (Figures 5.2.4, 5.2.5 and 5.2.6), and iii) blank reactions (Figures 5.2.7, 5.2.8, 5.2.9 and 5.2.10).

The main purposes of this section are to establish reaction in both the ambient and elevated pressure reaction vessels, and compare the hydrogenation rate and product distributions in the ambient and elevated pressure reaction vessels. This section is also intended to check if there is any significant difference between final product distribution, hydrogenation rates and reaction profile when programmed and non-programmed reduction are employed with the 1% Pd/C catalyst.

Latter sections of this chapter detail logical extensions of these reactions with variables such as the catalyst weight, catalyst and reaction reagent. The vast majority of the experiments listed here used a 1% Pd/C catalyst supplied by ICI Synetix. It was selected as being representative of heterogeneous catalysts used in fine chemical applications [5, 6, 7, 8].

i) Ambient Pressure Reactions

Tables 5.2.1 and 5.2.2 detail a summary of the reaction data, and Figures 5.2.1 and 5.2.2 shows reaction profiles for ambient pressure reactions employing the 1% Pd/C catalyst with 2-butyne-1,4-diol and *cis*-2-butene-1,4-diol respectively. Table 5.2.3 details a summary of the reaction data, and Figure 5.2.3 shows a reaction profile for an ambient pressure reaction employing non-programmed reduction of the 1% Pd/C catalyst and 2-butyne-1,4-diol. When programmed reduction of the catalyst is employed with the ambient pressure vessel the catalyst is reduced *in*-situ in the gas phase. With non-programmed reduction the catalyst is reduced *in-situ* in the liquid phase (detailed in Section 3.5). The reason for using programmed reduction of the catalyst is that, although palladium catalysts can be reduced in the liquid phase at room temperature, other catalysts such as supported copper catalysts can not. To allow for comparison between both supported palladium and supported copper catalysts the bulk of the reactions in this thesis are conducted with programmed reduction of catalyst (unless otherwise stated).

The experimental procedure for Figures 5.2.1 and 5.2.2 was the same as that detailed in Section 3.5 for an ambient pressure reaction that employed a programmed reduction of the catalyst. Figure 5.2.3 employed non-programmed reduction of the catalyst to see if there was any significant difference the programmed and non-programmed reduction procedures with respect reaction rate and product distribution. Figures 5.2.1 and 5.2.3 reached a conversion of the 2-butyne-1,4-diol of 96.00% in 720 minutes and 95.90% in 720 minutes respectively. A selectivity in the order of 95% towards the formation of *cis*-2-butene-1,4-diol was maintained during the course of the reaction until 96.00% and 95.90% conversion of 2-butyne-1,4-diol for Figures 5.2.1 and 5.2.3 respectively. Figure 5.2.2 reached a conversion of *cis*-2-butene-,4-diol of 99.04% in 720 minutes. For Figure 5.2.2 the selectivity towards butane-1,4-diol hydrogenation was unexpectedly low with it peaking at 30.81% after 60 minutes, and being in the order of 10% or lower during the course of the reaction.

Most importantly, there was no significant difference observed between the reaction profiles and hydrogenation rate for the programmed and non-programmed reduction of the catalyst in Figures 5.2.1 and 5.2.3 respectively (see Table 5.2). The initial rate of hydrogenation of 2-butyne-1,4-diol for Figures 5.2.1 and 5.2.3 was 1.96×10^{-5} and 1.83×10^{-5} moles/l/s/g catalyst. The initial rate of hydrogenation for *cis*-2-butene-1,4-diol for Figure 5.2.2 was 1.74×10^{-5} mole/l/s/g catalyst. The major product for Figures 5.2.1, 5.2.2 and 5.2.3 at the end of the reaction was iso-propoxytetrahydrofuran, followed closely by butane-1,4-diol. The final mass-balances for Figures 5.2.1, 5.2.2 and 5.2.3 were 70.61%, 67.29% and 70.91% respectively. The mass-balance plots for Figure 5.2.1 and 5.2.2 can be seen in Figure 5.2.11 a) and b) respectively.

ii) Elevated Pressure Reactions

Tables 5.2.4 and 5.2.5 detail a summary of the reaction data, and Figures 5.2.4 and 5.2.5 shows reaction profiles for elevated pressure reactions employing the 1% Pd/C catalyst with 2-butyne-1,4-diol and *cis*-2-butene-1,4-diol respectively. Table 5.2.6 details a summary of the reaction data, and Figure 5.2.6 shows a reaction profile for an elevated pressure reaction employing non-programmed reduction of the 1% Pd/C catalyst and 2-butyne-1,4-diol.

The experimental procedure for Figures 5.2.4 and 5.2.5 was the same as that detailed in Section 3.6 for an elevated pressure reaction that employed a programmed *ex*-situ reduction of the catalyst (reduction of catalyst in the gas phase). Figure 5.2.6 employed non-programmed *in-situ* reduction (reduction of the catalyst in the liquid phase) as detailed in Section 3.6, to see if there was any significant difference the programmed and non-programmed reduction procedures with respect reaction rate and product distribution. Figures 5.2.4 and 5.2.6 reached a conversion of the 2-butyne-1,4-diol of 96.29% in 120 minutes and 96.76% in 120 minutes respectively. A selectivity in the order of 95% towards the formation of *cis*-2-butene-1,4-diol was maintained during the course of the reaction until 96.29% and 96.76%

conversion of 2-butyne-1,4-diol for Figures 5.2.4 and 5.2.6 respectively. Figure 5.2.5 reached a conversion of *cis*-2-butene-,4-diol of 98.77% in 120 minutes. For Figure 5.2.5 the selectivity towards butane-1,4-diol hydrogenation was unexpectedly low with it peaking at 24.13% after 10 minutes, and being in the order of 10% or lower during the course of the reaction.

Again, there was no significant difference observed between the reaction profiles and hydrogenation rates for Figures 5.2.4 and 5.2.6 (See Table 5.2). The initial rate of hydrogenation of 2-butyne-1,4-diol for Figures 5.2.4 and 5.2.6 was 3.07×10^{-5} and 2.98×10^{-5} moles/l/s/g catalyst. The initial rate of hydrogenation for *cis*-2-butene-1,4-diol for Figure 5.2.5 was 2.55×10^{-5} mole/l/s/g catalyst.

As with ambient pressure reactions in i) there was formation of iso-propoxytetrahydrofuran observed during the course of the reaction for Figures 5.2.4, 5.2.5 and 5.2.6. There was also the formation of 1-(2-propanyloxy)-butan-1-ol that was not produced in the ambient pressure reactions in this section. The possible route to the formation of 1-(2-propanyloxy)-butan-1-ol is discussed in Chapter 6. The final product distributions for Figures 5.2.4, 5.2.5 and 5.2.6 are similar to those produced in the ambient pressure reactions. As with Figures 5.2.1, 5.2.2 and 5.2.3 the major product at the end of the reaction for Figures 5.2.4, 5.2.5 and 5.2.6 was iso-propoxytetrahydrofuran, followed closely by butane-1,4-diol. The final mass-balances for Figures 5.2.4, 5.2.5 and 5.2.6 were 64.77%, 64.12% and 62.09% respectively. The mass-balance plots for Figure 5.2.4 and 5.2.5 can be seen in Figure 5.2.11 c) and d) respectively. The mass-balance plots for Figure 5.2.3 and 5.2.6 are not included in Figure 5.2.11 because of their similarities to Figure 5.2.1 and 5.4.1 respectively.

Table 5.2 Comparison between activation procedure and initial reaction rates for ambient and elevated pressure reactions.

Reaction	Reaction reagent	Reactor	Catalyst activation type	Initial rate (moles/l/s/g catalyst)
Figure 5.2.1	2-butyne-1,4-diol	Ambient	Programmed (*in-situ*, gas phase reduction)	1.96×10^{-5}
Figure 5.2.3	2-butyne-1,4-diol	Ambient	Non-programmed (*in-situ*, liquid phase reduction	1.83×10^{-5}
Figure 5.2.4	2-butyne-1,4-diol	Elevated	Programmed (*ex-situ*, gas phase reduction)	3.07×10^{-5}
Figure 5.2.6	2-butyne-1,4-diol	Elevated	Non-programmed (*in-situ*, liquid phase reduction	2.98×10^{-5}

From Table 5.2 we can see that both the ambient and elevated pressure reactions in this section illustrate the ease of activation of palladium for these types of hydrogenation reactions. The initial rates of hydrogenation for the two ambient pressure reactions detailed in Table 5.2, 1.96×10^{-5} and 1.83×10^{-5} moles/l/s/g catalyst for Figures 5.2.1 and 5.2.2 respectively. The initial rates for Figures 5.2.1 and 5.2.2 are very close to each other, the same observation can be made for the elevated pressure reactions. It is experimentally easier to adopt a non-programmed *in-situ* activation of the 1% Pd/C catalyst. This is unique to palladium catalysts. It is not possible to activate a supported copper catalyst in the same manner, they require programmed activation of the catalyst (Section 5.9).

iii) Blank Reactions

Blank reactions were conducted to ensure that any observed reaction could be solely attributed to the presence of the 1% Pd/C catalyst and not occur on the carbon support, or homogeneously in the reaction solvent. Figure 5.2.7 and 5.2.8 are profiles for test reactions that were conducted using only the catalyst support instead of the catalyst in the ambient and elevated pressure reaction vessels respectively. In both Figure 5.2.7 and 5.2.8 the carbon support underwent a programmed reduction as detailed in Sections 3.5 and 3.6 for ambient and elevated pressure reactions respectively. The carbon support proved to be completely inactive in both the ambient and elevated pressure test reactions. Figure 5.2.9 and 5.2.10 are profiles for test reactions that were conducted with no solid present (*i.e.* Pd/C or carbon support) in the ambient and elevated pressure reaction vessels respectively. Both Figure 5.2.9 and 5.2.10 showed the solvent to be completely inactive to hydrogenation without the presence of the catalyst, with no observed reaction.

Table 5.2.1 Ambient pressure reaction employing the 1% Pd/C catalyst

Time (minutes)	Butyne-1,4-diol (moles/l)	Butene-1,4-diol (moles/l)	Butane-1,4-diol (moles/l)	Butanol (moles/l)	*Cis*-crotyl alcohol (moles/l)	*T*-crotyl alcohol (moles/l)	3-butene-1-ol (moles/l)	Iso-propoxythf (moles/l)	Conversion (%)	Selectivity (%)
0	0.2351	0	0	0	0	0	0	0	0	0
30	0.2258	0.0071	0	0	0	0	0	0	3.97	76.40
60	0.2179	0.0163	0	0	0	0	0	0	7.31	94.75
90	0.2159	0.0192	0	0	0	0	0	0.0001	8.16	99.92
120	0.2088	0.0254	0	0	0	0	0	0.0001	11.21	96.48
150	0.2034	0.0298	0	0	0	0	0	0.0002	13.50	93.78
180	0.1967	0.0363	0	0	0	0	0	0.0003	16.36	94.43
210	0.1916	0.0415	0	0	0.0036	0.0051	0	0.0004	18.49	95.52
240	0.1853	0.0473	0	0	0.0038	0.0055	0.0041	0.0005	21.20	95.00
270	0.1740	0.0567	0	0	0.0039	0.0065	0.0045	0.0007	26.01	92.68
300	0.1623	0.0694	0.0023	0	0.0040	0.0071	0.0047	0.0008	30.99	95.18
330	0.1590	0.0741	0.0026	0	0.0041	0.0079	0.0050	0.0010	32.36	97.38
360	0.1534	0.0811	0.0030	0	0.0042	0.0087	0.0053	0.0012	34.78	99.19
390	0.1389	0.0901	0.0032	0	0.0042	0.0091	0.0054	0.0012	40.91	93.66
420	0.1247	0.1035	0.0033	0	0.0043	0.0095	0.0055	0.0013	46.98	93.70
450	0.1156	0.1068	0.0035	0	0.0044	0.0097	0.0055	0.0014	50.83	89.34
480	0.1043	0.1244	0.0037	0	0.0044	0.0102	0.0056	0.0015	55.63	95.12
720	0.0094	0.2013	0.0080	0.0006	0.0066	0.0103	0.0070	0.0023	96.00	89.17
1440	0.0074	0.0150	0.0331	0.0290	0.0124	0.0092	0.0089	0.0378	96.84	6.57
1680	0.0075	0.0041	0.0396	0.0298	0.0145	0.0071	0.0099	0.0481	96.83	1.79
1800	0.0074	0.0048	0.0419	0.0308	0.0063	0.0070	0.0099	0.0483	96.84	2.12
2880	0.0074	0.0036	0.0432	0.0309	0.0149	0.0071	0.0099	0.0490	96.84	1.58

Figure 5.2.1 Reaction profile for an ambient pressure reaction employing the 1% Pd/C

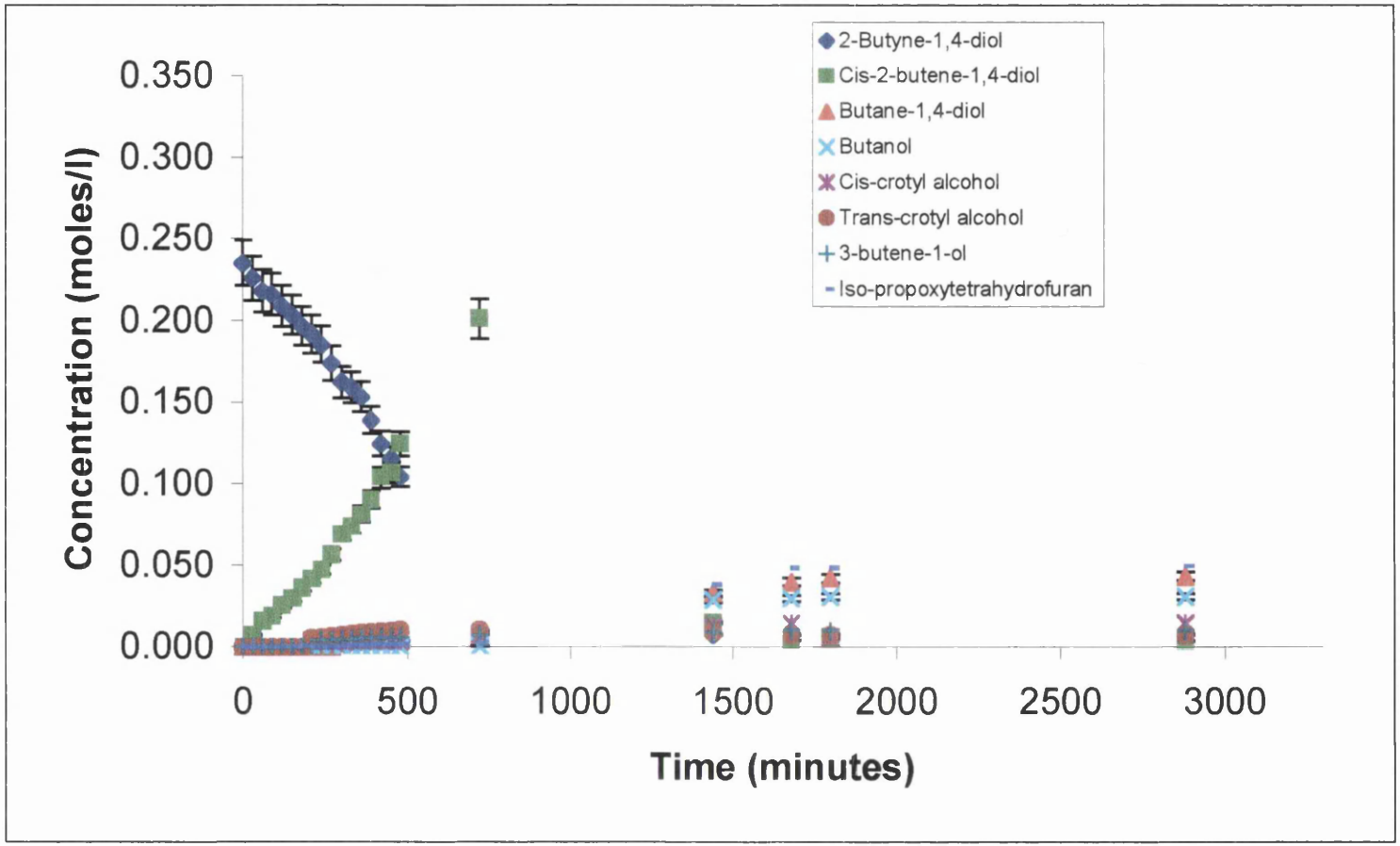


Table 5.2.2 Ambient pressure reaction employing the 1% Pd/C catalyst and *cis*-2-butene-1,4-diol

Time (minutes)	Butene-1,4-diol (moles/l)	Butane-1,4-diol (moles/l)	Butanol (moles/l)	*Cis*-crotyl alcohol (moles/l)	*T*-crotyl alcohol (moles/l)	3-butene-1-ol (moles/l)	Iso-propoxythf (moles/l)	Conversion (%)	Selectivity (%)
0	0.2270	0	0	0	0	0	0	0	0
60	0.2104	0.0051	0	0.0038	0.0055	0.0021	0.0039	7.30	30.81
120	0.2051	0.0054	0	0.0039	0.0059	0.0057	0.0126	9.65	24.85
180	0.1909	0.0065	0.0003	0.0040	0.0073	0.0071	0.0146	15.90	17.97
240	0.1844	0.0061	0.0005	0.0043	0.0080	0.0069	0.0203	18.77	14.33
300	0.1686	0.0074	0.0010	0.0043	0.0100	0.0080	0.0214	25.71	12.61
360	0.1364	0.0083	0.0016	0.0044	0.0126	0.0084	0.0283	39.94	9.11
420	0.1160	0.0089	0.0028	0.0045	0.0134	0.0093	0.0328	48.89	8.03
480	0.1036	0.0133	0.0051	0.0045	0.0152	0.0087	0.0395	54.37	10.80
540	0.0626	0.0132	0.0110	0.0047	0.0187	0.0091	0.0418	72.41	8.00
600	0.0140	0.0258	0.0171	0.0110	0.0268	0.0074	0.0495	93.83	12.13
660	0.0028	0.0282	0.0207	0.0204	0.0228	0.0086	0.0519	98.78	12.58
720	0.0022	0.0438	0.0285	0.0136	0.0075	0.0084	0.0517	99.04	19.50
900	0.0019	0.0445	0.0260	0.0125	0.0071	0.0091	0.0507	99.18	19.78
1000	0.0013	0.0447	0.0264	0.0131	0.0071	0.0092	0.0510	99.43	19.80

Figure 5.2.2 Reaction profile for an ambient pressure reaction employing the 1% Pd/C catalyst and *cis*-2-butene-1,4-diol

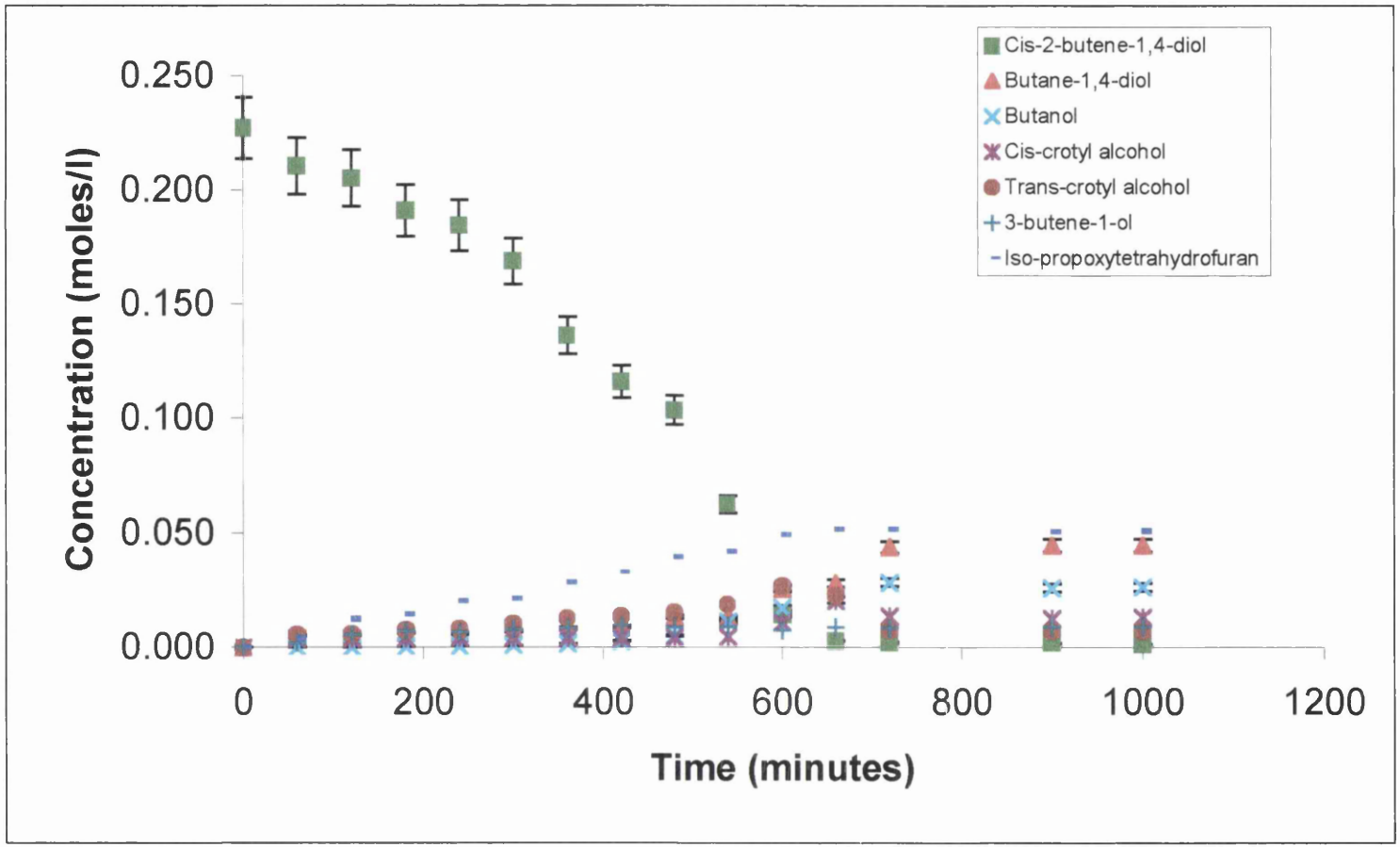


Table 5.2.3 Ambient pressure reaction employing the 1% Pd/C catalyst (employing non-programmed reduction of the catalyst)

Time (minutes)	Butyne-1,4-diol (moles/l)	Butene-1,4-diol (moles/l)	Butane-1,4-diol (moles/l)	Butanol (moles/l)	*Cis*-crotyl alcohol (moles/l)	*T*-crotyl alcohol (moles/l)	3-butene-1-ol (moles/l)	Iso-propoxythf (moles/l)	Conversion (%)	Selectivity (%)
0	0.2341	0	0	0	0	0	0	0	0	0
30	0.2263	0.0078	0	0	0	0	0	0	3.35	99.95
60	0.2169	0.0162	0	0	0	0	0	0	7.34	94.17
90	0.2153	0.0184	0	0	0	0	0	0	8.03	97.79
120	0.2096	0.0238	0	0	0	0	0	0	10.49	97.03
150	0.1966	0.0298	0	0	0	0	0	0.0002	16.03	79.47
180	0.1967	0.0343	0	0	0	0	0	0.0003	16.00	91.68
210	0.1925	0.0416	0	0	0.0037	0.0049	0	0.0003	17.76	99.98
240	0.1822	0.0467	0	0	0.0037	0.0053	0.0037	0.0003	22.18	90.01
270	0.1743	0.0578	0	0	0.0038	0.0055	0.0042	0.0006	25.56	96.51
300	0.1592	0.0702	0.0024	0	0.0037	0.0075	0.0043	0.0007	32.00	93.75
330	0.1543	0.0722	0.0027	0	0.0040	0.0076	0.0047	0.0010	34.11	90.40
360	0.1399	0.0815	0.0026	0	0.0038	0.0087	0.0047	0.0012	40.26	86.48
390	0.1386	0.0912	0.0032	0	0.0041	0.0081	0.0059	0.0012	40.79	95.51
420	0.1236	0.1054	0.0031	0	0.0042	0.0097	0.0054	0.0013	47.22	95.34
450	0.1173	0.1076	0.0036	0	0.0045	0.0099	0.0051	0.0014	49.90	92.10
600	0.0631	0.1654	0.0037	0	0.0041	0.0101	0.0058	0.0015	73.03	96.73
720	0.0096	0.2015	0.0082	0.0090	0.0053	0.0102	0.0072	0.0021	95.90	89.74
1440	0.0073	0.0143	0.0321	0.0231	0.0132	0.0093	0.0092	0.0378	96.87	6.29
1680	0.0073	0.0039	0.0352	0.0267	0.0134	0.0073	0.0104	0.0481	96.90	1.72
1900	0.0071	0.0051	0.0423	0.0310	0.0142	0.0071	0.0103	0.0479	96.96	2.25
2400	0.0072	0.0049	0.0425	0.0312	0.0142	0.0074	0.0105	0.0481	96.91	2.16

Figure 5.2.3 Reaction profile for an ambient pressure reaction employing the 1% Pd/C (employing solvent reduction of the catalyst)

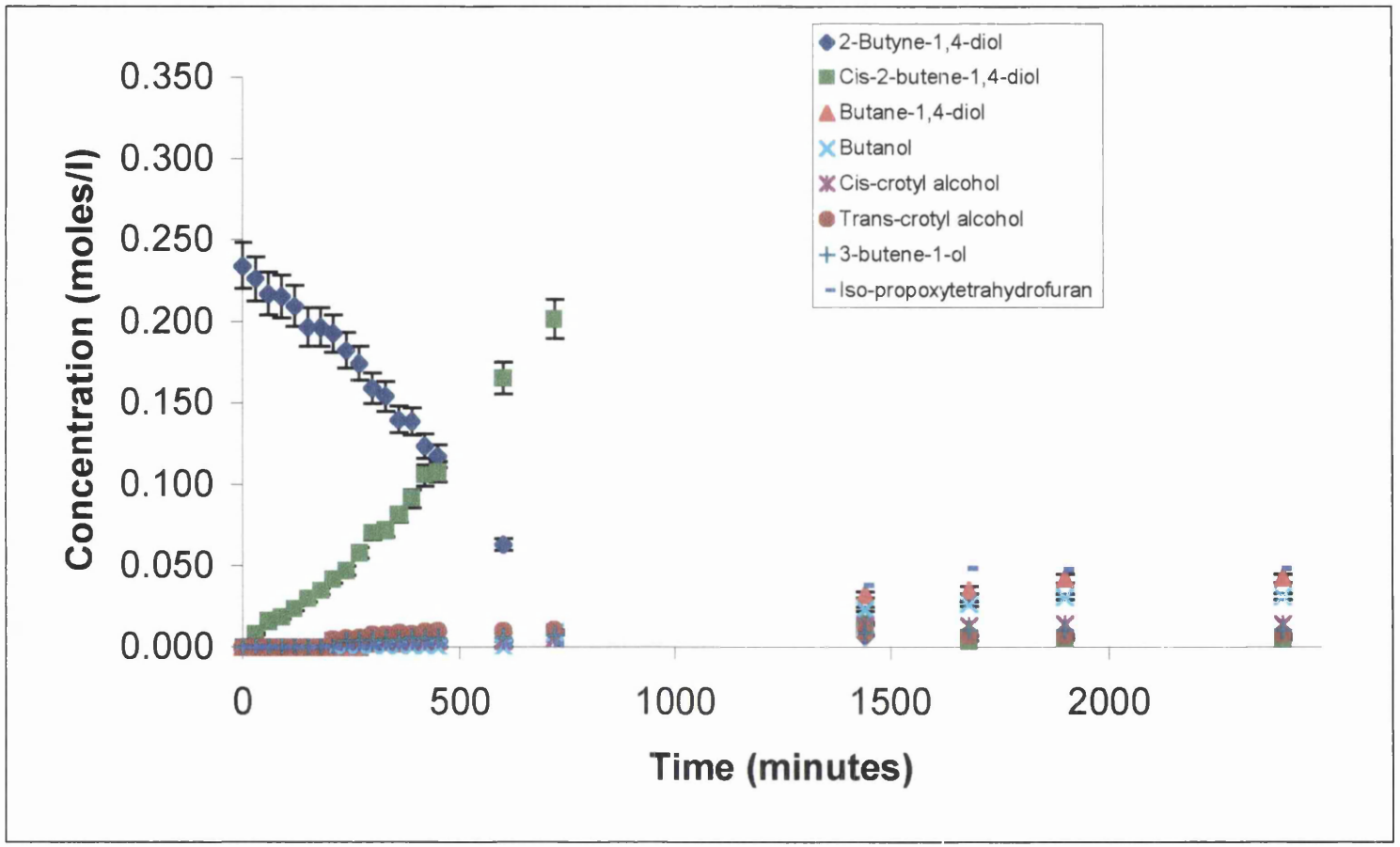


Table 5.2.4 Elevated pressure reaction employing the 1% Pd/C catalyst

Time (minutes)	Butyne-1,4-diol (moles/l)	Butene-1,4-diol (moles/l)	Butane-1,4-diol (moles/l)	Butanol (moles/l)	*Cis*-crotyl alcohol (moles/l)	*T*-crotyl alcohol (moles/l)	3-butene-1-ol (moles/l)	Iso-propoxythf (moles/l)	1-(2-propanyox) (moles/l)	Conversion (%)	Selectivity (%)
0	0.2358	0	0	0	0	0	0	0	0	0	0
15	0.2038	0.0271	0	0	0	0.0019	0.0048	0.0012	0	13.58	84.60
30	0.1709	0.0613	0.0035	0	0	0.0034	0.0049	0.0014	0	27.55	94.33
45	0.1290	0.0999	0.0044	0	0.0033	0.0059	0.0062	0.0024	0	45.30	93.51
60	0.1089	0.1221	0.0061	0	0.0033	0.0060	0.0063	0.0024	0	53.83	96.18
75	0.0721	0.1582	0.0104	0.0049	0.0066	0.0087	0.0114	0.0031	0	69.44	96.60
90	0.0219	0.1749	0.0146	0.0046	0.0064	0.0084	0.0110	0.0030	0.0003	90.73	81.73
105	0.0158	0.1706	0.0230	0.0142	0.0109	0.0084	0.0123	0.0181	0.0040	93.28	77.56
120	0.0087	0.1299	0.0306	0.0144	0.0110	0.0085	0.0124	0.0232	0.0012	96.29	57.18
135	0.0083	0.1143	0.0315	0.0197	0.0122	0.0066	0.0109	0.0287	0.0040	96.48	50.23
150	0.0080	0.0897	0.0351	0.0219	0.0133	0.0071	0.0117	0.0318	0.0047	96.62	39.36
180	0.0073	0.0373	0.0363	0.0261	0.0147	0.0085	0.0125	0.0443	0.0048	96.89	16.32
210	0.0073	0.0022	0.0375	0.0250	0.0142	0.0081	0.0122	0.0402	0.0049	96.89	0.98
240	0.0073	0.0017	0.0370	0.0245	0.0140	0.0081	0.0120	0.0399	0.0049	96.90	0.75
270	0.0072	0.0014	0.0374	0.0241	0.0136	0.0080	0.0119	0.0396	0.0048	96.93	0.61
300	0.0073	0.0014	0.0381	0.0243	0.0138	0.0080	0.0119	0.0405	0.0048	96.92	0.61
330	0.0073	0.0013	0.0367	0.0241	0.0137	0.0079	0.0118	0.0431	0.0048	96.90	0.59
360	0.0073	0.0013	0.0373	0.0249	0.0139	0.0080	0.0120	0.0404	0.0048	96.91	0.58
420	0.0073	0.0012	0.0416	0.0248	0.0138	0.0079	0.0119	0.0395	0.0048	96.92	0.53

Figure 5.2.4 Reaction profile for an elevated pressure reaction employing the 1% Pd/C catalyst

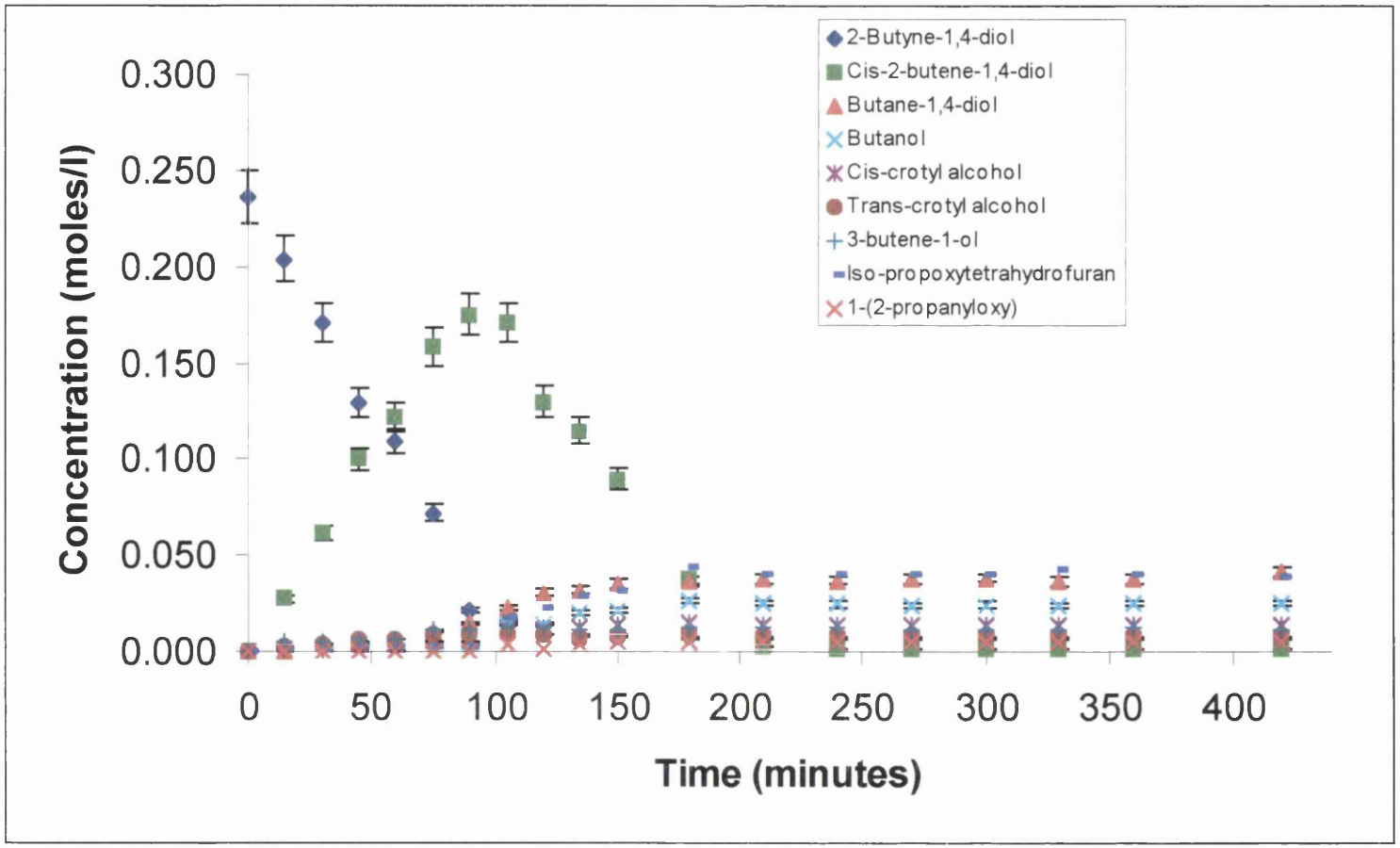


Table 5.2.5 Elevated pressure reaction employing the 1% Pd/C catalyst and *cis*-2-butene-1,4-diol

Time (minutes)	Butene-1,4-diol (moles/l)	Butane-1,4-diol (moles/l)	Butanol (moles/l)	*Cis*-crotyl alcohol (moles/l)	*T*-crotyl alcohol (moles/l)	3-butene-1-ol (moles/l)	Iso-propoxythf (moles/l)	1-(2-propanoxy) (moles/l)	Conversion (%)	Selectivity (%)
0	0.2330	0	0	0	0	0	0	0	0	0
10	0.2146	0.0044	0	0.0012	0.0051	0.0030	0.0037	0	7.90	24.13
20	0.2076	0.0047	0	0.0034	0.0055	0.0073	0.0112	0	10.91	18.65
30	0.1934	0.0059	0.0010	0.0039	0.0082	0.0088	0.0136	0	16.99	14.87
40	0.1838	0.0081	0.0006	0.0042	0.0072	0.0092	0.0193	0	21.13	16.49
50	0.1656	0.0069	0.0009	0.0042	0.0096	0.0096	0.0205	0	28.92	10.17
70	0.1405	0.0075	0.0016	0.0046	0.0123	0.0109	0.0295	0	39.70	8.12
80	0.1106	0.0079	0.0028	0.0045	0.0124	0.0109	0.0339	0.0006	52.52	6.44
90	0.0936	0.0111	0.0051	0.0046	0.0143	0.0110	0.0374	0.0009	59.83	7.94
100	0.0593	0.0119	0.0114	0.0048	0.0174	0.0120	0.0395	0.0009	74.54	6.82
110	0.0146	0.0231	0.0165	0.0107	0.0283	0.0109	0.0464	0.0014	93.74	10.59
120	0.0029	0.0195	0.0205	0.0201	0.0215	0.0117	0.0497	0.0036	98.77	8.48
180	0.0021	0.0368	0.0307	0.0131	0.0067	0.0118	0.0486	0.0041	99.10	15.94
195	0.0016	0.0379	0.0276	0.0125	0.0065	0.0119	0.0491	0.0046	99.29	16.40
240	0.0013	0.0386	0.0256	0.0123	0.0063	0.0120	0.0487	0.0046	99.43	16.67

Figure 5.2.5 Reaction profile for an elevated pressure reaction employing the 1% Pd/C catalyst and *cis*-2-butene-1,4-diol

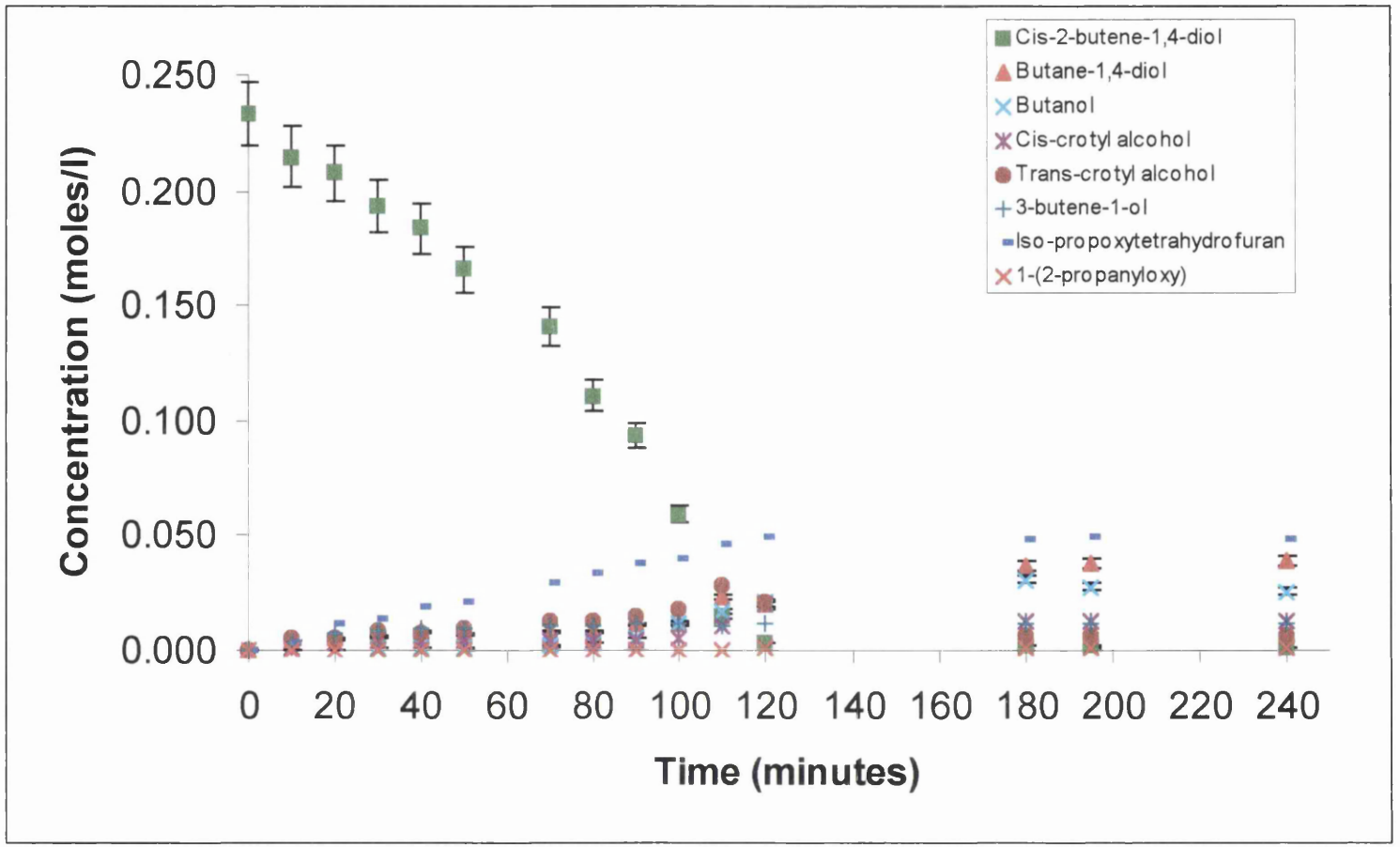


Table 5.2.6 Elevated pressure reaction employing the 1% Pd/C catalyst (employing non-programmed reduction of the catalyst)

Time (minutes)	Butyne-1,4-diol (moles/l)	Butene-1,4-diol (moles/l)	Butane-1,4-diol (moles/l)	Butanol (moles/l)	*Cis*-crotyl alcohol (moles/l)	*T*-crotyl alcohol (moles/l)	3-butene-1-ol (moles/l)	Iso-propoxythf (moles/l)	1-(2-propanyox) (moles/l)	Conversion (%)	Selectivity (%)
0	0.2406	0	0	0	0	0	0	0.0	0	0	0
15	0.2058	0.0318	0	0	0	0.0010	0.0023	0.0012	0	14.43	91.64
30	0.1700	0.0683	0.0023	0	0	0.0032	0.0032	0.0013	0	29.33	96.81
45	0.1290	0.1012	0.0043	0	0.0031	0.0056	0.0052	0.0022	0	46.37	90.72
60	0.1112	0.1241	0.0051	0	0.0031	0.0056	0.0053	0.0023	0	53.77	95.96
75	0.0732	0.1482	0.0104	0.0037	0.0062	0.0067	0.0100	0.0028	0	69.57	88.56
90	0.0224	0.1954	0.0146	0.0040	0.0060	0.0056	0.0101	0.0028	0.0003	90.69	89.57
105	0.0139	0.1600	0.0222	0.0132	0.0102	0.0078	0.0103	0.0165	0.0004	94.22	70.59
120	0.0078	0.1354	0.0306	0.0133	0.0103	0.0076	0.0104	0.0221	0.0012	96.76	58.17
135	0.0078	0.1100	0.0315	0.0187	0.0115	0.0076	0.0104	0.0261	0.0038	96.76	47.26
150	0.0079	0.0762	0.0351	0.0210	0.0124	0.0067	0.0113	0.0312	0.0045	96.72	32.77
180	0.0078	0.0321	0.0378	0.0241	0.0137	0.0078	0.0111	0.0402	0.0046	96.76	13.79
210	0.0079	0.0022	0.0378	0.0243	0.0133	0.0075	0.0113	0.0412	0.0046	96.72	0.96
270	0.0079	0.0013	0.0376	0.0244	0.0131	0.0075	0.0114	0.0412	0.0046	96.72	0.56
330	0.0081	0.0013	0.0377	0.0244	0.0129	0.0075	0.0114	0.0413	0.0046	96.63	0.56
420	0.0081	0.0013	0.0378	0.0244	0.0131	0.0075	0.0114	0.0414	0.0044	96.63	0.56

Figure 5.2.6 Reaction profile for an elevated pressure reaction employing the 1% Pd/C catalyst (employing solvent reduction of the catalyst)

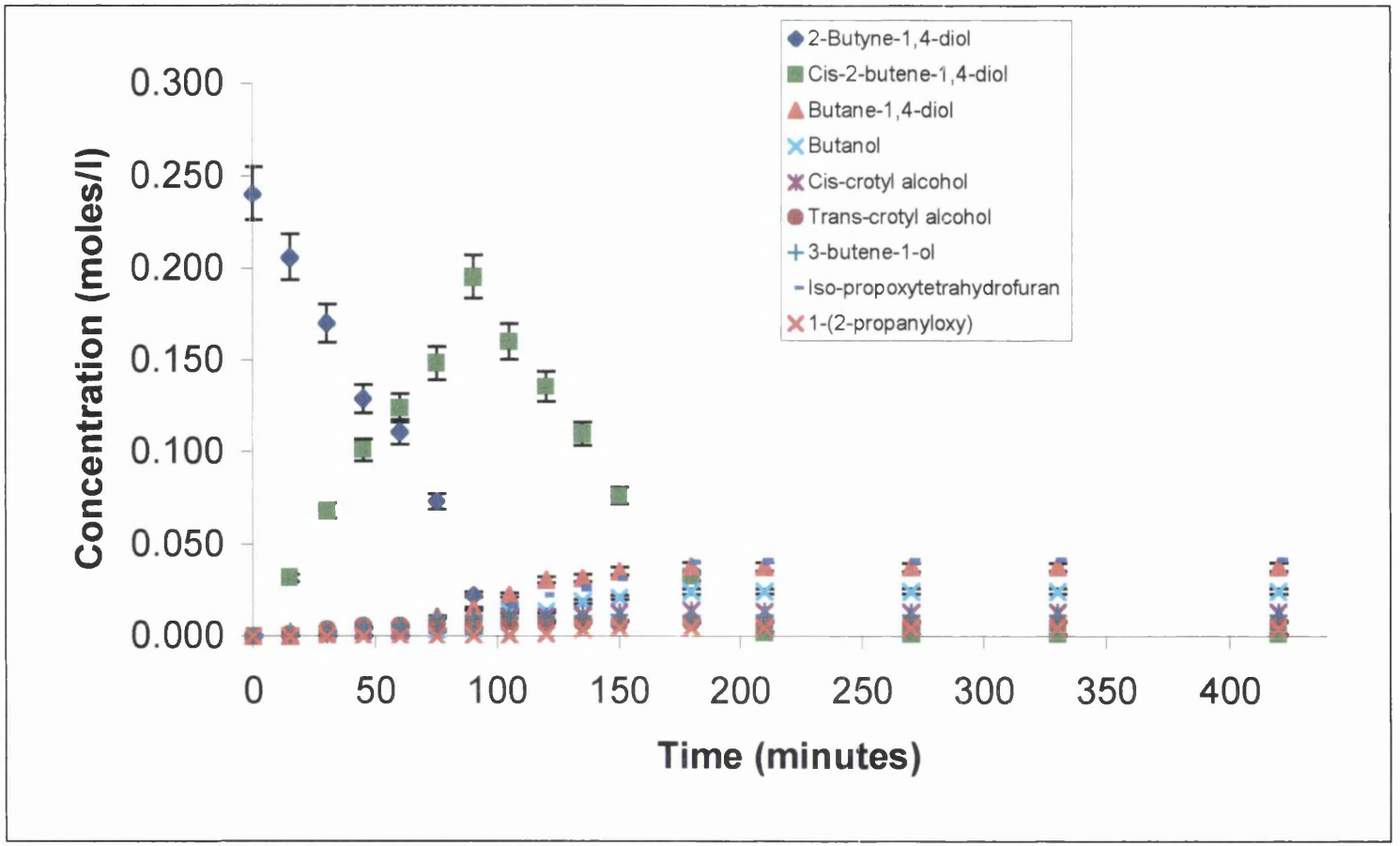


Table 5.2.7 Summary table for Section 5.2

Reaction	Reagent	Rate of reaction (moles/l/s/g catalyst)	T.O.F (moles/l/s/ Pd surface)	Final product order	Final % mass-balance	% Conversion at t=100 minutes	Time to full conversion (minutes)
Figure 5.2.1 (ambient)	2-butyne-1,4-diol	1.96×10^{-5}	3.62×10^{-24}	Iso-propoxythf, butane-1,4-diol, butanol and *cis*-crotyl alcohol	70.61	9.63	720
Figure 5.2.2 (ambient)	*Cis*-2-butene-1,4-diol	1.74×10^{-5}	3.22×10^{-24}	Iso-propoxythf, butane-1,4-diol, butanol and *cis*-crotyl alcohol	67.29	8.48	720
Figure 5.2.3 (ambient)	2-butyne-1,4-diol	1.83×10^{-5}	3.38×10^{-24}	Iso-propoxythf, butane-1,4-diol, butanol and *cis*-crotyl alcohol	70.91	8.85	720
Figure 5.2.4 (elevated)	2-butyne-1,4-diol	3.07×10^{-5}	5.67×10^{-24}	Iso-propoxythf, butane-1,4-diol, butanol and *cis*-crotyl alcohol	64.77	92.43	120
Figure 5.2.5 (elevated)	*Cis*-2-butene-1,4-diol	2.55×10^{-5}	4.71×10^{-24}	Iso-proproxythf, butane-1,4-diol, butanol and *cis*-crotyl alcohol	64.12	74.54	120
Figure 5.2.6 (elevated)	2-butyne-1,4-diol	2.98×10^{-5}	5.51×10^{-24}	Iso-proproxythf, butane-1,4-diol, butanol and *cis*-crotyl alcohol	62.09	93.04	120

Figure 5.2.7 Reaction profile for ambient pressure reaction employing the the carbon support

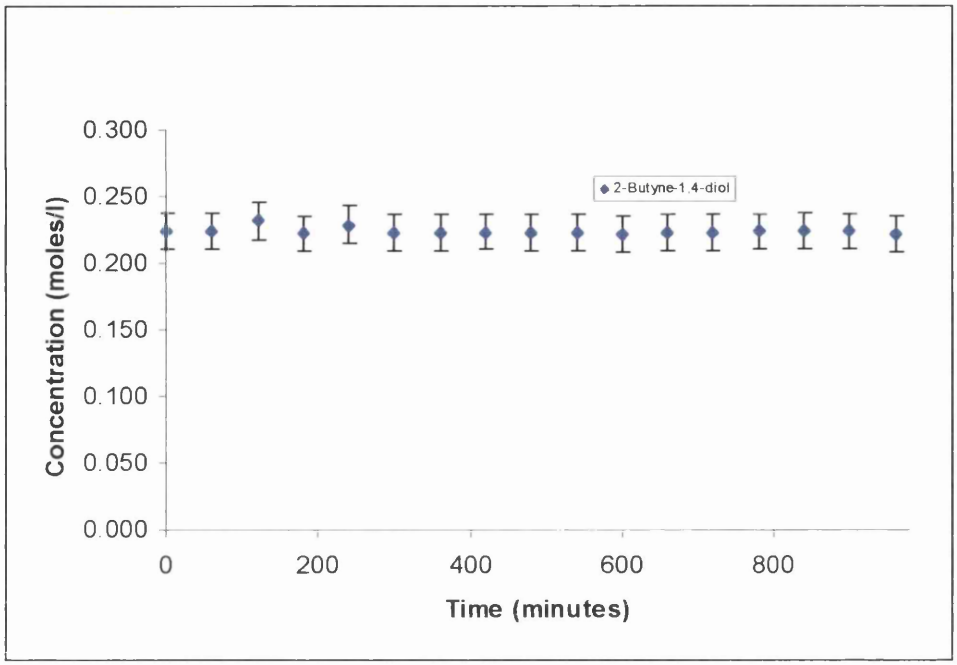


Figure 5.2.8 Reaction profile for elevated pressure reaction employing the the carbon support

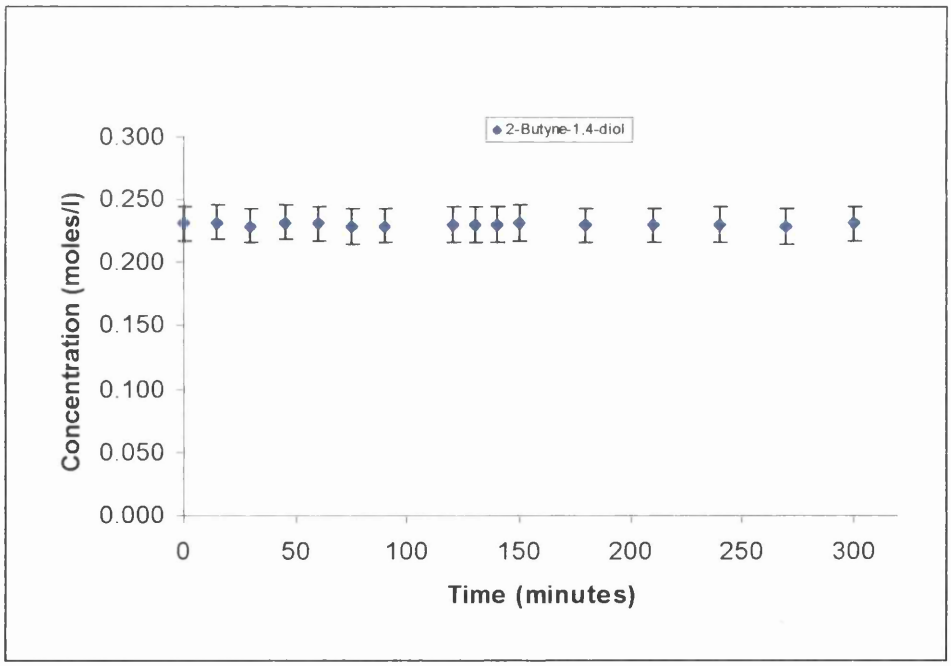


Figure 5.2.9 Reaction profile for ambient pressure reaction with no catalyst present

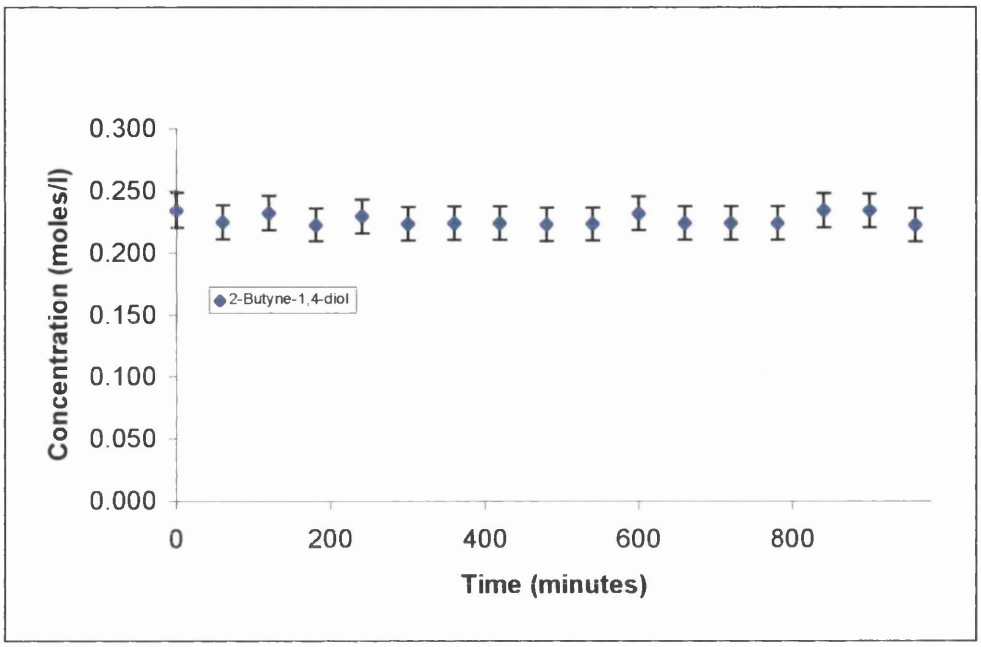


Figure 5.2.10 Reaction profile for elevated pressure reaction with no catalyst present

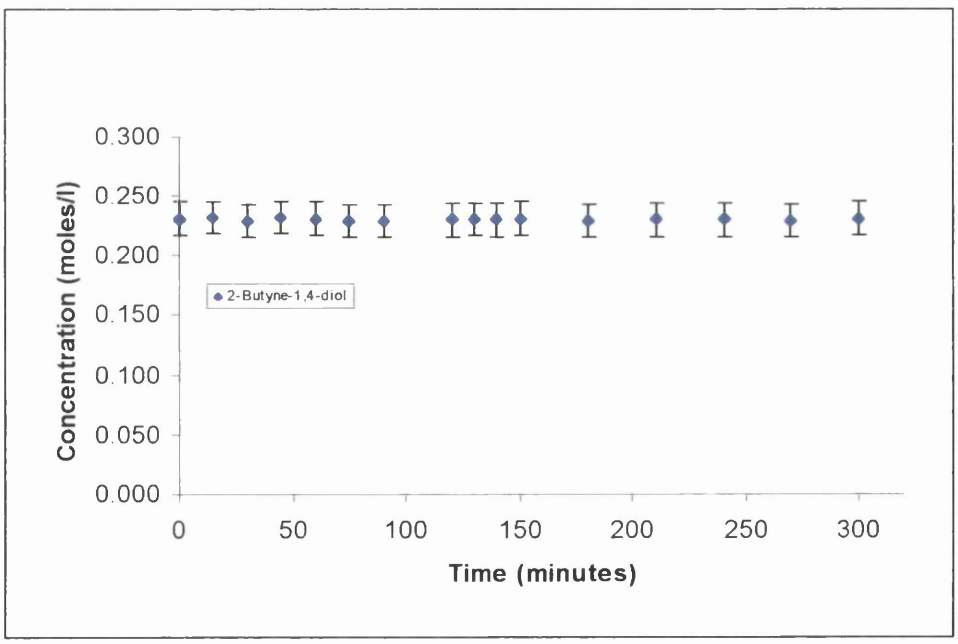
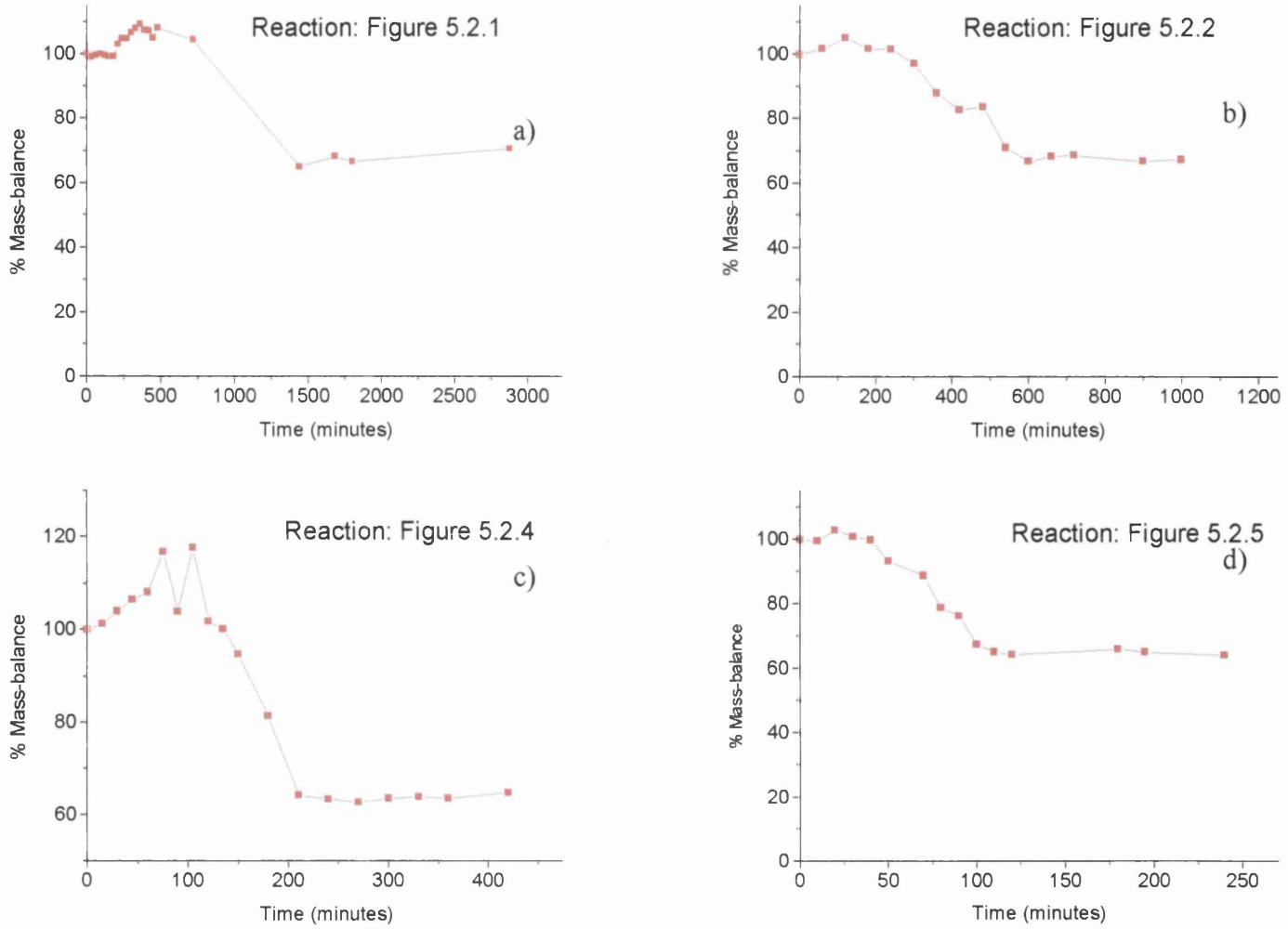


Figure 5.2.11 Mass-balances for reactions from Section 5.2



5.2.1 Discussion for ambient and elevated pressure reactions

In the experiments in this section reaction has been successfully established for the ambient and elevated pressure reaction vessels, the ambient and elevated pressure reactions in this section are benchmark experiments by which other catalysts and reagents can be compared to. All the ambient and elevated pressure reactions in this section show a number of products that would not be expected from work detailed in the literature when employing the 1% Pd/C catalyst [9]. The products that would not be expected from the ambient pressure reactions are 3-buten-1-ol and iso-propoxytetrahydrofuran. The products that would not be expected from the elevated pressure reactions are 3-buten-1-ol and iso-propoxytetrahydrofuran and 1-(2-propanyloxy)-butan-1-ol. In all the reactions in this section 3-buten-1-ol is likely to be formed from derived for a isomerisation on the surface of the catalyst of either *cis* or *trans*-crotyl alcohol. The possible formation mechanism for iso-propoxytetrahydrofuran in the ambient pressure reactions, and iso-propoxytetrahydrofuran and 1-(2-propanyloxy)-butan-1-ol in the elevated pressure reactions is discussed in more detail in Chapter 6.

Comparing both the ambient and elevated pressure experiments in this section that detail the selective hydrogenation of 2-butyne-1,4-diol and *cis*-2-butene-1,4-diol, it can be seen that the increase in pressure between the ambient and elevated pressure reactions does not have a significant effect on the final product distributions (with the order of the major products being same, Table 5.2.7) . There is however the presence of 1-(2-propanyloxy)-butan-1-ol in the elevated pressure reactions (Figure 5.2.4, 5.2.5 and 5.2.6) that is not observed in the ambient pressure reaction (Figure 5.2.1, 5.2.2 and 5.2.3). This formation of 1-(2-propanyloxy)-butan-1-ol is probably due to the increased pressure in the elevated pressure reaction vessel (more discussion about the formation of 1-(2-propanyloxy)-butan-1-ol can be found in Chapter 6).

Looking at Table 5.2.7 we can see an increased rate of hydrogenation when comparing the elevated with the equivalent ambient pressure reactions. The rate of 2-butyne-1,4-diol hydrogenation increases from $1.96x10^{-5}$ to $3.07x10^{-5}$ moles/l/s/g catalyst when comparing Figure 5.2.1 with Figure 5.2.4. A similar rate increase in hydrogenation rate can be seen by comparing Figure 5.2.2 and Figure 5.5.5, from $1.74x10^{-5}$ to $2.55x10^{-5}$ moles/l/s/g catalyst. There was also a correspond increase in T.O.F. This increased reaction rate and T.O.F. was due to the increased pressure that the elevated pressure reaction vessel operates under.

It should be noted that the rates detailed here are in moles/l/s/g catalyst, they have been normalised by concentration, and catalyst mass, they have not been normalised for total of moles of reaction reagent that were present in the reaction vessel. This can give a misleading impression of the actual rate of hydrogenation in the elevated pressure reaction vessel, with it appearing lower than it actually is. The amount of catalyst mass, reaction reagent and propan-2-ol is four times greater in the elevated pressure reaction vessel, each of their respect quantities have been scaled up equally to allow for comparisons between the ambient and elevated pressure reaction vessels. It can be seen clearly from the reaction profiles that for the ambient and elevated pressure reactions that in the elevated pressure reaction vessel the reaction rate is approximately 6 times faster, with it taking only approximately 120 minutes to fully hydrogenate the 2-butyne-1,4-diol and *cis*-2-butene-1,4-diol present in the reaction vessel, as opposed to the equivalent reactions in the ambient pressure reaction vessel that require approximately 720 to fully hydrogenated 2-butyne-1,4-diol and *cis*-2-butene-1,4-diol.

The values for % conversion at t=100 minutes are another way to illustrate the increased hydrogenation rate in the elevated pressure reaction vessel, when comparing the ambient and elevated pressure reactions (Table 5.2.7). At t=100 minutes the % conversions for Figure 5.2.1, 5.2.2 and 5.2.3 are 9.63, 8.48 and 8.85% respectively. For the equivalent reactions in the elevated pressure reaction vessel, At t=100 minutes the % conversions for Figure 5.2.4, 5.2.5 and 5.2.6 are 92.43, 74.54 and 93.04% respectively. Clearly the elevated

pressure reaction allows for a greater degree of conversion of the reaction reagent in a shorter period of time. From Table 5.2.7 it can be seen that the rates of hydrogenation of *cis*-2-butene-1,4-diol (Figures 5.2.2 and 5.2.5) are slower than those for 2-butyne-1,4-diol (5.2.1 and 5.2.4) in the same reaction vessel.

There was relatively little hydrogenation of *cis*-2-butene-1,4-diol when there was still 2-butyne-1,4-diol available in the reaction vessel for hydrogenation in the ambient and elevated pressure reactions. If we look at the ambient and elevated pressure reactions that employed *cis*-2-butene-1,4-diol we can see a variety of "side products" e.g. *cis* and *trans*-crotyl alcohol, 3-buten-1-ol, butanol, iso-propoxytetrahydrofuran (and in the elevated pressure reaction vessel 1-(2-propanoyloxy)-butan-1-ol) being formed in greater concentrations than they were in reactions that employed 2-butyne-1,4-diol, during the initial stages of the reaction. This suggests that the reaction products are derived form *cis*-2-butene-1,4-diol, rather than directly from 2-butyne-1,4-diol.

The reason that the rates of hydrogenation of 2-butyne-1,4-diol and formation of *cis*-2-butene-1,4-diol do not correspond exactly is because there is minor amounts of the *cis*-2-butene-1,4-diol is able to access the active sites on the catalyst surface in Figures 5.2.1, 5.2.3, 5.2.4 and 5.2.6. This is reflected in the selectivity to *cis*-2-butene-1,4-diol formation. It is around 95% for all the reaction in this section that employ 2-butyne-1,4-diol as the reaction reagent, up to full conversion of 2-butyne-1,4-diol. If the rates of hydrogenation of 2-butyne-1,4-diol and formation of *cis*-2-butene-1,4-diol varied considerably, it would be indicative of *cis*-2-butene-1,4-diol being converted into the other products observed in the reaction profile, when there was still 2-butyne-1,4-diol present in the reaction vessel. The rates are not different enough when taken in conjunction with the values for the selectivity to *cis*-2-butene-1,4-diol conversion to show that there is significant hydrogenation/reaction of *cis*-2-butene-1,4-diol when there is still 2-butyne-1,4-diol present in the reaction vessel. *Cis*-2-butene-1,4-diol can be thought as a hub through which the formation of all the other reaction products can commence.

Comparing the selectivity for the hydrogenation of 2-butyne-1,4-diol in the ambient and elevated pressure reactions, with the selectivity of the hydrogenation of *cis*-2-butene-1,4-diol in the ambient and elevated pressure reactions, illustrates an interesting point. After the initial period the selectivity to the formation of *cis*-2-butene-1,4-diol formation is over 95% in both the ambient and elevated pressure reactions. The selectivity towards the formation of butane-1,4-diol for the hydrogenation of *cis*-2-butene-1,4-diol in both the ambient and elevated pressure reaction vessels in the order of 10% or lower. Butane-1,4-diol was chosen for to base the selectivity on because it involves the gain of two hydrogen atoms in a *cis*-2-butene-1,4-diol molecule, as does the hydrogenation of 2-butyne-1,4-diol to *cis*-2-butene-1,4-diol. Butane-1,4-diol represents the next logical step for a sequential hydrogenation of 2-butyne-1,4-diol after it has been converted to *cis*-2-butene-1,4-diol. The low selectivity towards the formation of butane-1,4-diol (10% or less) in both the ambient and elevated pressure reactions illustrate the ability of the adsorbed *cis*-2-butene-1,4-diol species to be converted into butane-1,4-diol, but also the other "side products" (the "side products are butanol, *cis* and *trans*-crotyl alcohol, 3-buten-1-ol, iso-propoxytetrahydrofuran and 1-(2-propanyloxy)-butan-1-ol in the case of the elevated pressure reactions).

The first stage of the reaction can be thought of as the complete hydrogenation of 2-butyne-1,4-diol, *i.e.* 100% conversion. The second stage of the reaction can be thought of as when there is no further reaction occurring in the reaction vessel, *i.e.* 200% conversion. The hydrogenation reactions in this section for 2-butyne-1,4-diol show high selectivity towards the formation of *cis*-2-butene-1,4-diol (circa 95%) in the first stage of the reaction. In the second of the reaction there is low selectivity towards the formation of butane-1,4-diol (10% or less), hence the formation of the other "side products". The *cis*-2-butene-1,4-diol hydrogenation reactions mirror the second stage of the 2-butyne-1,4-diol hydrogenation, with low selectivity towards butane-1,4-diol.

If we consider the mass-balances on Figure 5.2.11 we can see they are not complete. The ambient pressure reactions, Figures 5.2.1 and 5.2.2 have 70.61% and 67.29% final mass-balances respectively. The elevated pressure

reactions, Figures 5.2.4 and 5.2.5 have 64.77% and 64.12% final mass balances respectively. Clearly some of the starting reagent is being converted into some species that can not be easily detected using the GC set-up that was employed for this project. Subsequent work conducted by Iain Duncanson has found using superior GC apparatus, that this deficit in the mass-balance is due to the formation of butane and butene during the course of the reaction [10]. Any mass-inbalance with the 1% Pd/C catalyst can be attributed to the formation of butane and butene during the course of the reaction.

Figures 5.2.7 and 5.2.8 show that there is no reaction when the 1% Pd/C catalyst has been substituted for the carbon support in the ambient and elevated pressure reaction vessels respectively. Figures 5.2.9 and 5.2.10 show that there is no reaction when there is no reaction when there is no catalyst present in the reaction vessel in the ambient and elevated pressure reaction vessels respectively.

5.2.2 SUMMARY FOR SECTION 5.2

- Reaction has been established for the ambient and elevated pressure reaction vessels, we have benchmark reactions by which we can compare other catalysts and reagents.

- Iso-propoxytetrahydrofuran is an unexpected (major) product at the end of the reactions in this section that is likely to be formed through a solvent interaction.

- The final product distributions for the ambient and elevated pressure reaction vessels are essentially the same (with the exception of 1-(2-propanyloxy)-butan-1-ol produced in the elevated pressure reaction vessel).

- Hydrogenation rate and T.O.F. increase form the ambient to elevated pressure reaction vessels, with the increase in pressure.

- Reduction of the 1% Pd/C catalyst by non-programmed reduction does not yield significantly different reaction profiles, hydrogenation rates and final product distributions, when compared with experiments that employed programmed reduction.

- When there is 2-butyne-1,4-diol still present in the reaction vessel, very little if any, hydrogenation of *cis*-2-butene-1,4-diol occurs.

- There was no reaction observed without the catalyst present.

- There was 95% selectivity towards *cis*-butene-1,4-diol formation, but only 10% selectivity towards butane-1,4-diol formation from *cis*-2-butene-1,4-diol.

- The mass-imbalance was due to the formation of butane and butene.

5.3 COMPETITIVE ADSORPTION EXPERIMENTS

This section summarises reactions that were conducted at ambient pressure to investigate the issue of competitive adsorption. Competitive adsorption studies are of interest, because they give an insight into the reaction mechanisms that occur at the catalyst surface. Competitive-adsorption studies have been performed to ascertain if the rate of 2-butyne-1,4-diol hydrogenation to *cis*-2-butene-1,4-diol is affected by the addition of a known amount of *cis*-2-butene-1,4-diol to the reaction solution, at the start of the reaction. Evaluation of reaction rates as the proportion of alkynediol and alkenediol is varied will provide insight into the relative adsorption coefficients of the two adsorbents on the Pd/C catalyst.

Indirectly, these studies also provide information on the distribution of active sites. If there is just one type of active site on the catalyst surface then the addition of *cis*-2-butene-1,4-diol to the reaction mixture may encourage competitive adsorption of the 2-butyne-1,4-diol and *cis*-2-butene-1,4-diol at the active site on the catalyst surface, the rate of butyne-1,4-diol hydrogenation may be affected. If there are two different types of sites at the catalyst surface, then the addition of *cis*-2-butene-1,4-diol to the reaction mixture will not affect the rate at which the 2-butyne-1,4-diol is hydrogenated, the two sites can act independently from each other. There may however be only one main active site that is responsible for 2-butyne-1,4-diol hydrogenation to *cis*-2-butene-1,4-diol (and the other products) and *cis*-2-butene-1,4-diol hydrogenation to butane-1,4-diol (and the other products). If this is the case then this could be explained by the fact that the heat of adsorption for butyne-1,4-diol is more favourable to that of the *cis*-2-butene-1,4-diol (*i.e.* 2-butyne-1,4-diol is more strongly bound to the catalyst surface).

In studies reported in the literature the selectivity that is observed during alkyne hydrogenation is attributed to the stronger adsorption of the alkyne compared to that of the alkene [11, 12, 13, 14. 15]. It was found in ultra-high vacuum acetylene adsorbs more strongly than ethylene [16]. The adsorption

coefficients for alkynes are always higher than those for alkenes [53]. This leads to preference of their hydrogenations in competitive hydrogenations.

Tables 5.3.1 and 5.3.2 detail a summary of the reaction data, and Figures 5.3.1 and 5.3.2 shows reaction profiles for ambient pressure reactions employing the 1% Pd/C catalyst with an alkyne:alkene ratio of 1:1 and 2:1 respectively.

The experimental procedure for Figures 5.3.1 and 5.3.2 were essentially the same as that detailed in Section 3.5 for an ambient pressure reaction that employed a programmed *in-situ* reduction of the catalyst. The main differences from the reaction procedure stated in Section 3.5 were the concentrations of the starting solutions. For Figure 5.3.1 a reaction solution with a concentration of 0.233molar 2-butyne-1,4-diol and 0.227molar *cis*-2-butene-1,4-diol was employed, for Figure 5.3.2 a reaction solution with a concentration of 0.233molar 2-butyne-1,4-diol and 0.114molar *cis*-2-butene-1,4-diol was employed. Table 5.3.3 has summary data for other competitive adsorption experiments that were conducted.

As with the ambient pressure reactions that employed the 1% Pd/C catalyst for the hydrogenation of 2-butyne-1,4-diol, in Figures 5.3.1 and 5.3.2 there was formation of iso-propoxytetrahydrofuran observed during the course of the reaction. Iso-propoxytetrahydrofuran was present in smaller amounts than would be expected for a reaction that had no *cis*-2-butene-1,4-diol present at the start of the reaction. In both Figures 5.2.1 and 5.2.1 there was suppression of the other products that would not have been seen at the end of the reaction if there had been no addition of the *cis*-2-butene-1,4-diol in the starting reaction solution, e.g. iso-propoxytetrahydrofuran was not the major product at the end of the reaction. Full hydrogenation of the 2-butyne-1,4-diol was effectively reached in approximately 720 minutes for both Figures 5.3.1 (96.66% conversion by 720 minutes) and 5.3.2 (96.79% conversion by 720 minutes), this compares favourably with the length of time that is required to fully hydrogenate the 2-butyne-1,4-diol when there is no addition of *cis*-2-butene-1,4-diol at the start of the reaction. Both Figures 5.3.1 and 5.3.2 had

high selectivity towards *cis*-2-butene-1,4-diol formation. Figure 5.3.1 had in the order of 92% selectivity to *cis*-2-butene-1,4-diol until 86.59% conversion, and Figure 5.3.2 had in the order 97% selectivity to *cis*-2-butene-1,4-diol until 79.42% conversion of 2-butyne-1,4-diol. These selectivities compare favourably with the selectivities from Section 5.2.

The rate of hydrogenation of 2-butyne-1,4-diol was 2.08×10^{-5} and 2.09×10^{-5} moles/l/s/g catalyst for Figures 5.3.1 and 5.3.2 respectively. The major product at the end of the reaction was *cis*-2-butene-1,4-diol, instead of iso-propoxytetrahydrofuran as it had been in Section 5.2, this is because the reactions were stopped before all the cis-2-butene-1,4-diol had been allowed to hydrogenate. The final mass balance for Figures 5.3.1 and 5.3.2 was 101.07% and 97.96% respectively, these compare well with the mass balance for Figure 5.2.1 at only around 70.61%.

Table 5.3.1 Ambient pressure reaction employing the 1% Pd/C catalyst, competitive adsorption experiment (1) (1:1 Alkyne:Alkene ratio)

Time (minutes)	Butyne-1,4-diol (moles/l)	Butene-1,4-diol (moles/l)	Butane-1,4-diol (moles/l)	Butanol (moles/l)	*Cis*-crotyl alcohol (moles/l)	*T*-crotyl alcohol (moles/l)	3-buten-1-ol (moles/l)	Iso-propoxythf (moles/l)	Conversion (%)	Selectivity (%)
0	0.2327	0.2226	0	0	0	0	0	0	0	0
60	0.2009	0.2520	0.0025	0	0	0.0008	0	0	13.63	100.94
120	0.1783	0.2716	0.0025	0	0	0.0012	0	0	23.36	94.87
180	0.1628	0.2849	0.0058	0	0	0.0023	0	0	30.01	92.99
240	0.1479	0.2984	0.0064	0	0	0.0045	0	0	36.44	92.44
300	0.1182	0.3272	0.0069	0	0	0.0048	0	0.0003	49.18	93.72
360	0.1046	0.3411	0.0079	0	0	0.0050	0	0.0003	55.06	94.53
420	0.0858	0.3551	0.0079	0.0011	0	0.0052	0	0.0005	63.12	92.03
480	0.0624	0.3738	0.0087	0.0018	0	0.0052	0.0000	0.0005	73.16	90.37
540	0.0456	0.3884	0.0092	0.0039	0	0.0056	0.0022	0.0007	80.38	90.06
600	0.0312	0.4005	0.0099	0.0067	0.0023	0.0058	0.0038	0.0008	86.59	89.61
660	0.0174	0.3973	0.0110	0.0174	0.0053	0.0060	0.0039	0.0008	92.53	82.37
720	0.0078	0.4014	0.0110	0.0234	0.0056	0.0062	0.0039	0.0010	96.66	80.65

Figure 5.3.1 Reaction profile for ambient pressure reaction employing the 1% Pd/C, competitive adsorption experiment (1) (1:1 Alkyne:Alkene ratio)

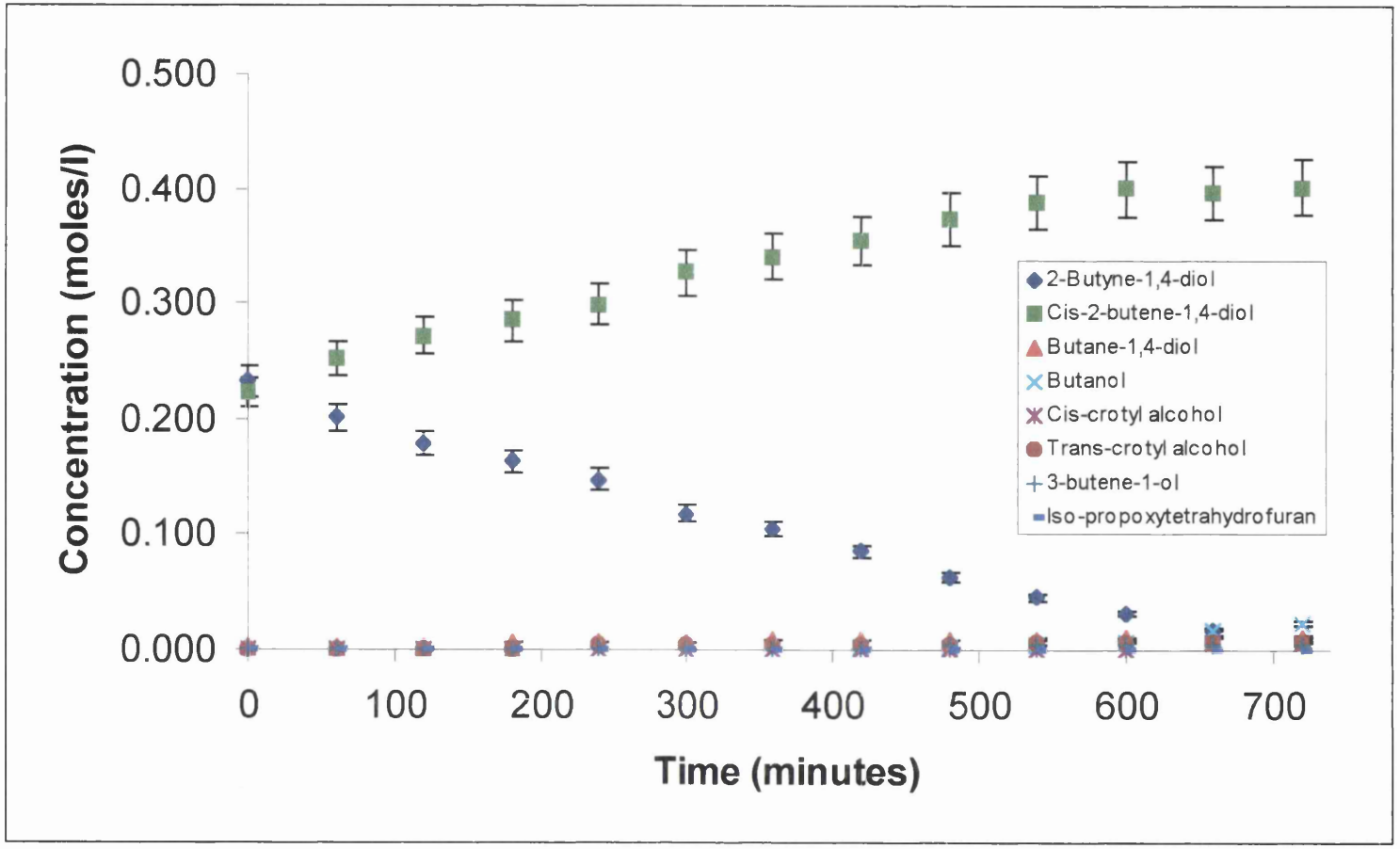


Table 5.3.2 Ambient pressure reaction employing the 1%Pd/C catalyst, competitive adsorption experiment (2) (2:1 Alkyne:Alkene ratio)

Time (minutes)	Butyne-1,4-diol (moles/l)	Butene-1,4-diol (moles/l)	Butane-1,4-diol (moles/l)	Butanol (moles/l)	*Cis*-crotyl alcohol (moles/l)	*T*-crotyl alcohol (moles/l)	3-buten-1-ol (moles/l)	Iso-propoxythf (moles/l)	Conversion (%)	Selectivity (%)
0	0.2333	0.1176	0	0	0	0	0	0	0	0
60	0.1984	0.1537	0	0	0	0	0	0	14.96	96.45
120	0.1719	0.1790	0	0	0	0	0	0	26.32	96.11
180	0.1628	0.1895	0.0047	0	0	0	0	0	30.20	98.60
240	0.1511	0.1988	0.0046	0	0	0.0039	0	0	35.24	95.81
300	0.1182	0.2325	0.0065	0	0	0.0046	0	0	49.32	97.77
360	0.1013	0.2486	0.0065	0	0	0.0048	0	0	56.56	97.43
420	0.0858	0.2584	0.0074	0.0001	0	0.0048	0	0.0002	63.22	93.87
480	0.0480	0.2973	0.0078	0.0001	0	0.0050	0.0038	0.0003	79.42	95.72
540	0.0424	0.2917	0.0086	0.0002	0.0012	0.0054	0.0039	0.0003	81.81	89.97
600	0.0312	0.2955	0.0095	0.0025	0.0022	0.0056	0.0038	0.0004	86.63	86.84
660	0.0164	0.2923	0.0101	0.0092	0.0048	0.0057	0.0039	0.0004	92.96	79.45
720	0.0075	0.2963	0.0104	0.0142	0.0050	0.0058	0.0039	0.0007	96.79	78.09

Figure 5.3.2 Reaction profile for an ambient pressure reaction employing the 1% Pd/C, competitive adsorption experiment (2) (2:1 Alkyne:Alkene ratio)

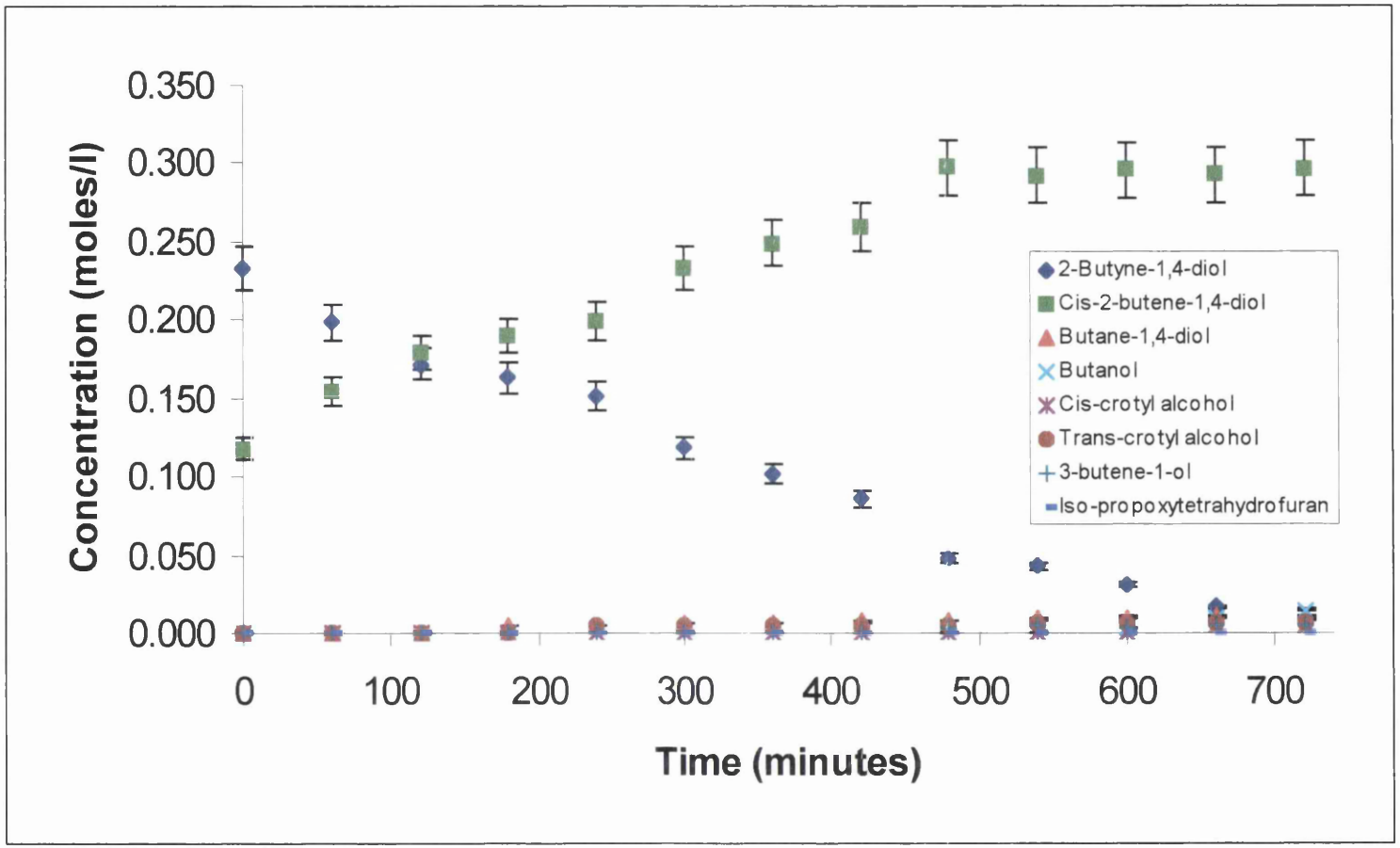


Table 5.3.3. Summary table of competitive adsorption experiments

2-Butyne-1,4-diol conc. (mol/l)	*Cis*-2-butene-1,4-diol conc. (mol/l)	[alkyne]:[alkene] ratio	2-butyne-1,4-diol use (mol/l/s/g catalyst)	*Cis*-2-butene-1,4-diol formation (mol/l/s/g catalyst)	Catalyst weight (g)
0.233	0.057	4:1	1.887×10^{-05}	1.741×10^{-05}	0.2503
0.174	0.057	3:1	1.862×10^{-05}	1.543×10^{-05}	0.2510
0.233	0.114	2:1	2.092×10^{-05}	1.686×10^{-05}	0.2508
0.116	0.057	2:1	1.892×10^{-05}	1.731×10^{-05}	0.2505
0.233	0.170	1:0.75	1.815×10^{-05}	1.723×10^{-05}	0.2506
0.174	0.114	1.5:1	1.906×10^{-05}	1.774×10^{-05}	0.2500
0.174	0.114	1.5:1	1.931×10^{-05}	1.101×10^{-05}	0.2497
0.233	0.227	1:1	2.082×10^{-05}	1.290×10^{-05}	0.2506
0.233	0.227	1:1	1.891×10^{-05}	1.683×10^{-05}	0.2507
0.174	0.170	1:1	1.884×10^{-05}	1.651×10^{-05}	0.2507
0.116	0.114	1:1	1.876×10^{-05}	1.721×10^{-05}	0.2499
0.058	0.057	1:1	2.123×10^{-05}	1.717×10^{-05}	0.2510
0.058	0.057	1:1	1.893×10^{-05}	1.724×10^{-05}	0.2499
0.116	0.170	1:1.5	1.843×10^{-05}	1.713×10^{-05}	0.2505
0.058	0.114	1:2	1.892×10^{-05}	1.727×10^{-05}	0.2506
0.116	0.227	1:2	1.910×10^{-05}	1.647×10^{-05}	0.2503
0.058	0.170	1:3	1.854×10^{-05}	1.766×10^{-05}	0.2501
0.058	0.227	1:4	1.932×10^{-05}	1.731×10^{-05}	0.2507
0.058	0.227	1:4	2.081×10^{-05}	1.710×10^{-05}	0.2510
0.058	0.455	1:8	1.887×10^{-05}	1.685×10^{-05}	0.2504
0.023	0.227	1:10	2.012×10^{-05}	1.717×10^{-05}	0.2506
0.023	0.341	1:15	1.912×10^{-05}	1.751×10^{-05}	0.2503
0.233	0	0	1.796×10^{-05}	1.692×10^{-05}	0.2506
0.233	0	0	1.792×10^{-05}	1.731×10^{-05}	0.2508
0.233	0	0	1.843×10^{-05}	1.731×10^{-05}	0.2511
0	0.227	0	0	$*1.743 \times 10^{-05}$	0.2503
0	0.227	0	0	$*1.718 \times 10^{-05}$	0.2506

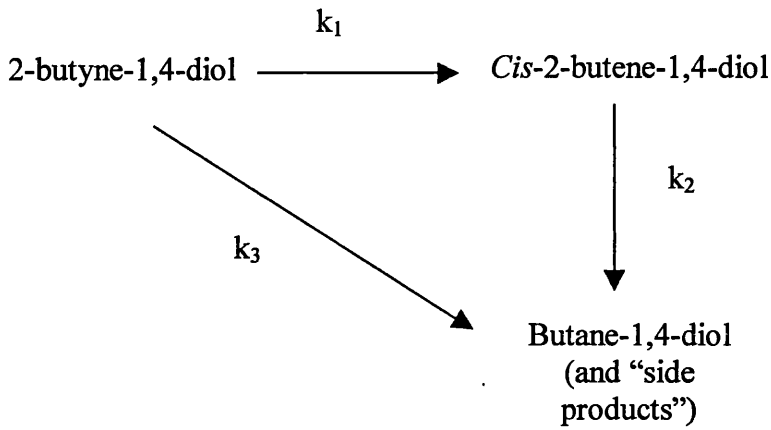
N.R. = normal reaction with no *cis*-2-butene-1,4-diol addition.

* Rate of hydrogenation of *cis*-2-butene-1,4-diol.

5.3.1 Discussion for competitive adsorption experiments

The results from the competitive adsorption study show the relative independence of the rate of 2-butyne-1,4-diol concentration with respect to *cis*-2-butene-1,4-diol concentration. This can be illustrated if we consider a simple Langmuir-Hinshelwood model [18] as described in Figure 5.3.4 below.

Figure 5.3.1 Simple reaction model for 2-butyne-1,4-diol hydrogenation



k_1=rate of hydrogenation of 2-butyne-1,4-diol to *cis*-2-butene-1,4-diol

k_2=rate of hydrogenation of *cis*-2-butene-1,4-diol to butane-1,4-diol and other products

k_3=rate of hydrogenation of 2-butyne-1,4-diol to butane-1,4-diol and other products

The rate constant that can be discounted from the above model is k_3, there is no evidence from the product distributions that 2-butyne-1,4-diol can form butane-1,4-diol and the other reaction products directly. Indeed, Figures 5.3.1 and 5.3.2 in this section, and Figures 5.2.1, 5.2.3, 5.2.4 and 5.2.6 in Section 5.2 show that when there is there is still 2-butyne-1,4-diol present in the

reaction vessel then there is very little formation of butane-1,4-diol and the "side products". Essentially the adsorption coefficient for 2-butyne-1,4-diol is greater than that for *cis*-2-butene-1,4-diol, when there is 2-butyne-1,4-diol present in the reaction vessel, the reaction/hydrogenation of *cis*-2-butene-1,4-diol is almost completely retarded.

There seems to be only one major type of active site on the catalyst surface and that 2-butyne-1,4-diol is more favourably bound to the site than *cis*-2-butene-1,4-diol. This demonstrated by the data detailed on the summary table (Table 5.3.3), the rate of 2-butyne-1,4-diol use does not (significantly) change with increasing or decreasing concentrations of *cis*-butene-1,4-diol. If there was true competitive adsorption (*i.e.* almost identical heats of adsorption for both of the alkynes), which would lead to competition between 2-butyne-1,4-diol and *cis*-2-butene-1,4-diol for the active sites on the catalyst surface, then an increase in the concentration of *cis*-2-butene-1,4-diol should illicit a decrease in the rate of 2-butyne-1,4-diol hydrogenation. A single site model, that is active for hydrogenation is illustrated by the experiments that were conducted using *cis*-2-butene-1,4-diol (detailed in Section 5.2). As with the ambient pressure reactions that employ the 1% Pd/C catalyst but do not have additions of *cis*-2-butene-1,4-diol, the rate of hydrogenation of *cis*-2-butene-1,4-diol is very slow when there is still 2-butyne-1,4-diol present in the reaction vessel that is available for hydrogenation. With the competitive-adsorption experiments the rate of *cis*-2-butene-1,4-diol hydrogenation is slower. *Cis*-2-butene-1,4-diol does not start to react noticeably until all the 2-butyne-1,4-diol has been hydrogenated (this can also be observed in the sudden drop in selectivity to *cis*-2-butene-1,4-diol observed in the reactions in this study when the 2-butyne-1,4-diol has been hydrogenated).

The experiments in Section 5.2 and this section both show that when there is still 2-butyne-1,4-diol available to be hydrogenated to the principal product, *i.e. cis*-2-butene-1,4-diol, then the rate of *cis*-2-butene-1,4-diol hydrogenation is very slow (almost negligible). If all the 2-butyne-1,4-diol has been hydrogenated (or as in the case of the reaction in section there is no 2-butyne-1,4-diol in the reaction solution at the beginning of the reaction), then *cis*-2-

butene-1,4-diol will be hydrogenated at a similar (but slower) rate to that which is observed for butyne-1,4-diol, around 1.75 $x10^{-5}$ as opposed to 1.95 $x10^{-5}$ moles/l/s.

If the rate of *cis*-2-butene-1,4-diol formation was significantly slower than the rate at which the 2-butyne-1,4-diol is hydrogenated, then you might suggest that the rate of *cis*-2-butene-1,4-diol formation observed was not the true rate of *cis*-2-butene-1,4-diol formation, but the rate of *cis*-2-butene-1,4-diol formation minus the rate at which it was be hydrogenated, because *cis*-2-butene-1,4-diol could be being hydrogenated. Under these circumstances it is possible that there would be a number of active surface sites that were responsible for the hydrogenation, *i.e.* site(s) for 2-butyne-1,4-diol hydrogenation and site(s) for *cis*-2-butene-1,4-diol hydrogenation. There could also be significant competitive hydrogenation between the 2-butyne-1,4-diol and the *cis*-2-butene-1,4-diol. The reactions clearly show that this is not the case, they show that there is only one major surface active site involved in the hydrogenation when there is 2-butyne-1,4-diol present, when all the 2-butyne-1,4-diol has been hydrogenated then the *cis*-2-butene-1,4-diol starts to get hydrogenated. The 2-butyne-1,4-diol is more strongly adsorbed to the catalyst surface than the *cis*-2-butene-1,4-diol as detailed in the literature [19, 20], when there is 2-butyne-1,4-diol in the reaction mixture then the 2-butyne-1,4-diol in preferentially hydrogenated before the *cis*-2-butene-1,4-diol, this also agrees with the literature [9, 19, 20, 21, 22, 23, 24], where when 2-butyne-1,4-diol was present in the reaction vessel, there was little or no hydrogenation of cis-2-butene-1,4-diol.

If the reactions in this section are allowed to continue until all the 2-butyne-1,4-diol is hydrogenated then the *cis*-2-butene-1,4-diol is hydrogenated and reacted, to produce similar final product distributions to the one in section 5.2. The reactions in this section and Section 5.2 show that *cis*-2-butene-1,4-diol is a crucial step in the formation of the other products, there is only minor formation of the other reaction products if there is 2-butyne-1,4-diol still present in the reaction vessel. There are no mass balance issues with the reactions in this section that were observed in Section 5.2, because none of the

reactions have been detailed up to the 200% conversion point. From the reactions in Section 5.2 it can be seen that the problems with the mass balance profile occur when all the 2-butyne-1,4-diol has be consumed, and *cis*-2-butene-1,4-diol is able to react to form the other "side products" and butene and butane that are the source of the mass balance issues. Since neither Figure 5.3.1 or 5.3.2 was allowed to continue until the *cis*-2-butene-1,4-diol had been substantially hydrogenated, there are no mass balance issues with the reactions detailed in this section.

5.4 REACTION ORDERS OF 2-BUTYNE-1,4-DIOL, *CIS*-2-BUTENE-1,4-DIOL AND CATALYST MASS

This section outlines reactions that were conducted at ambient pressure to determine the orders of reaction of 2-butyne-1,4-diol, *cis*-2-butene-1,4-diol and catalyst mass. The orders of reaction for these three reaction parameters can be determined by varying their respective amounts in a controlled manner.

The selective hydrogenation of 2-butyne-1,4-diol has been studied with a number of catalysts. There are few published literature studies that investigate the reaction orders of 2-butyne-1,4-diol and the catalyst mass (see Chapter 1). There are no available literature studies that investigate the effect on the rate of hydrogenation of 2-butyne-1,4-diol to *cis*-2-butyne-1,4-diol, with *cis*-2-butene-1,4-diol present at various concentrations when a carbon supported palladium catalyst is used. Only Chaudhari *et al* [21] has published data on how the concentration of *cis*-2-butene-1,4-diol effects the rate of 2-butyne-1,4-diol hydrogenation when a Pd-Zn/$CaCO_3$ catalyst is used. It was found that the having butene-1,4-diol present in the reaction vessel on hydrogenation of 2-butyne-1,4-diol did not effect the rate of 2-butyne-1,4-diol hydrogenation [21].

The reaction order with respect to hydrogen has been reported with different values. Chaudhari *et al* reported the reaction order to be ~0.5 with respect to hydrogen concentration [21]. Later work by Chaudhari *et al* [22] and Telkar *et al* [20] reported the initial rate of hydrogenation of 2-butyne-1,4-diol to have a linear dependence on catalyst loading and hydrogen pressure. Chaudhari *et al* [21] reported that the rate of hydrogenation of 2-butyne-1,4-diol varied linearly with the catalyst concentration, this is consistent with the absence of gas-liquid mass transfer. A similar statement was made by Telkar *et al* [20]. Chaudhari *et al* found that the initial 2-butyne-1,4-diol concentration had an adverse effect on the rate of hydrogenation at concentrations greater than 5% of 2-butyne-1,4-diol, but that at lower concentration the rate shows a zero order dependence on 2-butyne-1,4-diol concentration [21, 22].

From the literature evidence it is assumed that the reaction is first order with respect to hydrogen [20, 22]. The order of reaction experiments that are detailed in this section were all carried out using the 1% Pd/C catalyst in the ambient pressure reaction vessel. The reduction and reaction procedure in the same as those in Section 3.5 for an ambient pressure reaction, with the catalyst mass, and reagent concentration being varied as required.

Table 5.4.1 and Figure 5.4.1 detail the rate of *cis*-2-butene-1,4-diol formation against mass of catalyst. Table 5.4.1 also shows the number of palladium atoms that are equivalent to these catalyst masses, and the ratios of 2-butyne-1,4-diol molecules to surface palladium atoms for these experiments. From the results it can be seen that there is a linear dependence between reaction rate and the mass of catalyst that is used in the reaction. Bond illustrated that, a non-linear dependence of the reaction rate on catalyst mass, at a given stirring speed of agitation, indicates that the experimental system is limited by diffusion [25a]. Figure 5.4.1 shows the linearity of the relationship between the catalyst mass and the observed reaction rate, and therefore indicates that the reaction testing conducted over this range of catalyst mass is not diffusion limited. This means that measured rates are dictated by the rate of the reaction on the catalyst surface and, not the by the rate of reactants and products through the reaction medium [25b].

Table 5.4.2 and Figure 5.4.2 detail the rates of formation *cis*-2-butene-1,4-diol at different concentrations of 2-butyne-1,4-diol. The individual experiments showed a linear consumption of 2-butyne-1,4-diol, that lead to the corresponding formation of *cis*-2-butene-1,4-diol. Table 5.4.2 and Figure 5.4.2 show that the rate of hydrogenation of 2-butyne-1,4-diol remains effectively constant over the concentration rage of 0.0582 to 1.1630M.

The reaction order with respect to the concentration of one particular substance can be defined mathematically by Equation 5.4.1 [26].

Equation 5.4.1

$$\text{Order with respect to regent } X = \frac{\delta \log_{10} \text{rate}}{\delta \log_{10}[X]}$$

With this equation the reaction rate is evaluated under conditions such that the reaction variable are held constant [26]. This basically means that the gradient of the plot of log rate versus the log of a concentration of a particular species equals the reaction order.

Using Equation 5.4.1, the data detailed in Table 5.4.2 was processed; the results are given on Table 5.4.3 and Figure 5.4.3. These results show a near-zero reaction order rate in 2-butyne-1,4-diol, the gradient of the line being –0.0095. If we consider the experimental error, and the pattern shown during the individual experiments, the order with respect to 2-butyne-1,4-diol concentration can be said to be effectively zero. This is in agreement with the literature [20, 21, 22] at low concentrations of 2-butyne-1,4-diol.

The effect of *cis*-2-butene-1,4-diol upon the reaction rate was studied up to a concentration of 1.1364M, this gave a maximum ratio of 5:1 between *cis*-2-butene-1,4-diol and 2-butyne-1,4-diol. This is not a large concentration difference, but if the rates of reaction are taken in conjunction with the data in Table 5.3.3.1 it can be seen that the rate of hydrogenation of 2-butyne-1,4-diol and the rate of formation of *cis*-2-butene-1,4-diol are not significantly different up to ratios of 15:1 *cis*-2-butene-1,4-diol to 2-butyne-1,4-diol. The results are shown in Table 5.4.4 and Figure 5.4.4. This data was then processed to Equation 5.4.1, with the results being detailed in Table 5.4.5 and Figure 5.4.5.

These results show, as with the results for 2-butyne-1,4-diol, a near-zero reaction order rate in *cis*-2-butene-1,4-diol, the gradient of the line being –0.0047. If we consider the experimental error, the order with respect to *cis*-2-butene-1,4-diol concentration can be said to be effectively zero. There is no apparent adverse effect on the rate of hydrogenation of 2-butyne-1,4-diol when there is *cis*-2-butene-1,4-diol present in the reaction vessel. This is in agreement with Chaudhari *et al* findings for the effect on rate of hydrogenation of 2-butyne-1,4-diol with *cis*-2-butene-1,4-diol present in the reaction vessel [21].

In summary of the results discussed in this section, the hydrogenation of 2-butyne-1,4-diol over palladium catalysts was found to be zero order with respect to 2-butyne-1,4-diol concentration. The order in *cis*-2-butene-1,4-diol is found to be zero order also. There does not seem to be any retarding effect on the rate of hydrogenation of 2-butyne-1,4-diol by the presence of *cis*-2-butene-1,4-diol in the reaction vessel. Finally the reaction rates were found to increase linearly with the mass of catalyst, and the system was found to operate under kinetic control, *i.e.* not limited by diffusion [20], with no boundary layer associated problems [27, 28], if there were hydrogen pressure could decreases across the gas film due to film-diffusional resistance, hydrogen pressure could drop through the liquid film surrounding each H_2 bubble and again through the liquid film surrounding each catalyst particle (at the gas-liquid interface a concentration is established in accordance with Henry's law [29], $P_{hydrogen,\,g}=C_{hydrogen}H$, where C is concentration and H is the Henry's law constant (kPa m^3 $kmol^{-1}$)). This indicates validity of the ambient pressure reaction vessel as a means of evaluating different catalyst.

Therefore the rate equation for selective hydrogenation of 2-butyne-1,4-diol can be summed up by Equation 5.4.2:

Equation 5.4.2

$$\text{Rate} = k[\text{butynediol}]^0[H_2]^1[\text{catalyst}]^1$$

Table 5.4.1 Rate of *cis*-2-butene-1,4-diol formation vs. mass of catalyst at 338K

Mass of catalyst (g)	No. of surface metal atoms ($x10^{18}$)	Butyne:Pd^0 $_{surf.}$	Rate of *cis*-2-butene-1,4-diol formation (moles x 10^{-5}/l/s/g catalyst)
0	0	-	0
0.0025	0.014	828508.8	0.0173
0.0050	0.027	414254.4	0.0336
0.1000	0.541	20712.72	0.6712
0.1500	0.812	13808.48	0.9468
0.1500	0.812	13808.48	1.0068
0.2000	1.080	10356.36	1.2824
0.2000	1.080	10356.36	1.2224
0.2000	1.080	10356.36	1.3424
0.2500	1.350	8285.088	1.6920
0.2500	1.350	8285.088	1.7310
0.2500	1.350	8285.088	1.7320
0.3500	1.890	5917.92	2.1039
0.4000	2.160	5178.18	2.7244
0.4000	2.160	5178.18	2.5644
0.5000	2.710	4142.544	3.3000
0.5000	2.710	4142.544	3.3560
0.5000	2.710	4142.544	3.4560

Figure 5.4.1 Rate of *cis*-2-butene-1,4-diol formation vs. mass of catalyst at 338K

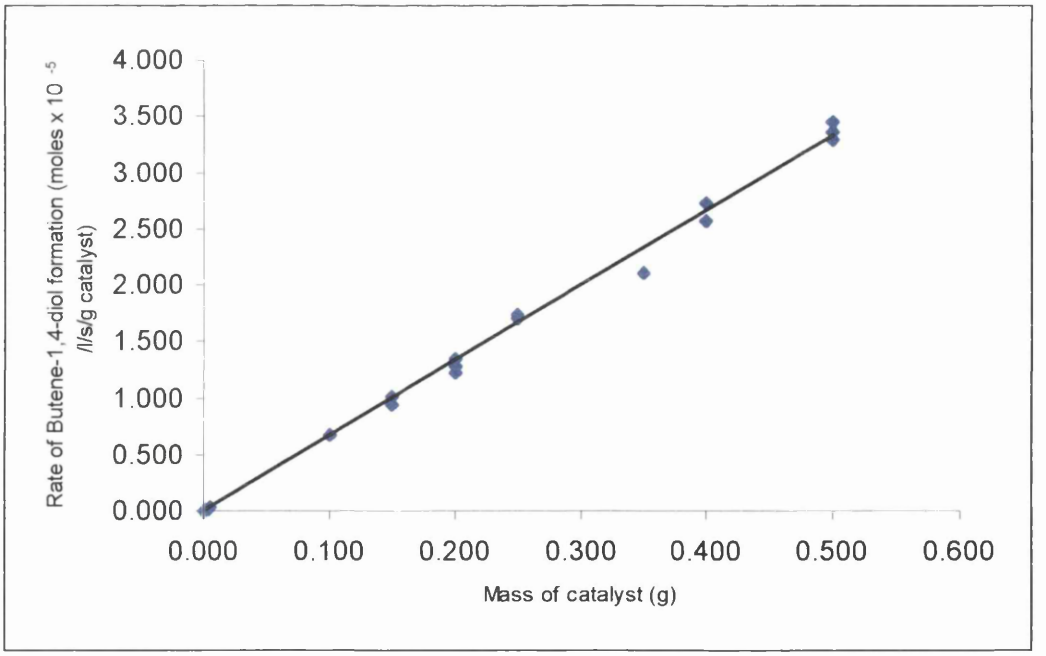


Table 5.4.2 Rate of *cis*-2-butene-1,4-diol formation vs. initial 2-butyne-1,4-diol concentration at 338K over 0.2500g 1% Pd/C catalyst

Initial 2-butyne-1,4-diol concentration (moles/l)	Rate of *cis*-2-butene-1,4-diol formation (moles x 10^{-5}/l/s/g catalyst)
0.0582	1.6921
0.1163	1.7211
0.2326	1.7231
0.2326	1.6711
0.2326	1.5512
0.3488	1.7110
0.4651	1.7312
1.1630	1.6512

Figure 5.4.2 Rate of *cis*-2-butene-1,4-diol formation vs. initial 2-butyne-1,4-diol concentration at 338K over 0.2500g 1% Pd/C catalyst

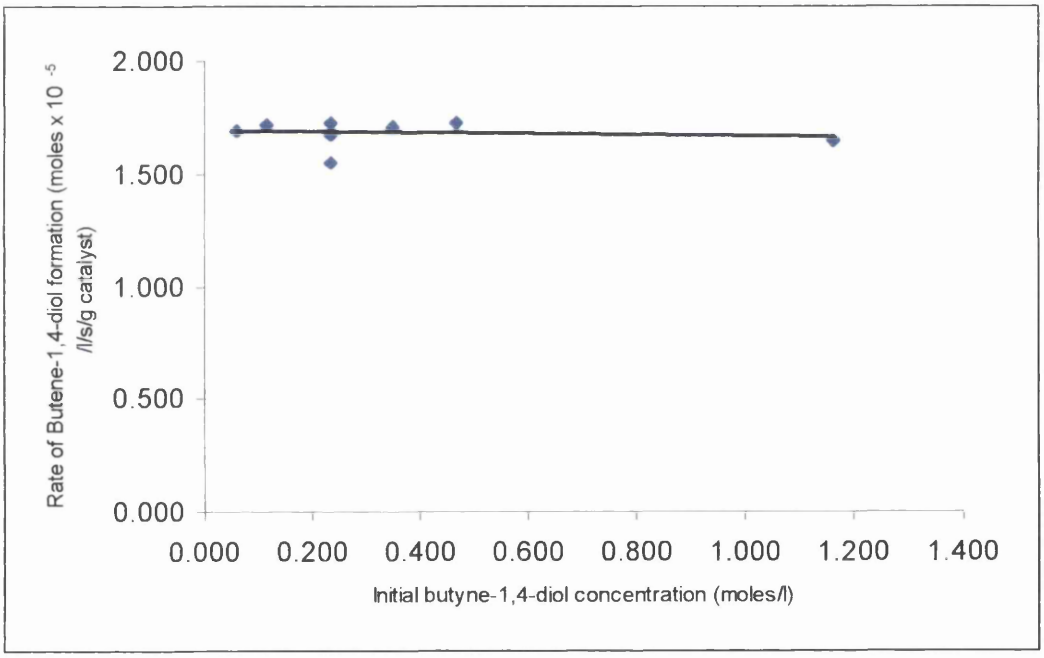


Table 5.4.3 Log (reaction rate) vs. log (2-butyne-1,4-diol concentration)

Log (2-butyne-1,4-diol concentration)	Log (reaction rate)
-1.2355	0.2284
-0.9344	0.2358
-0.6334	0.2363
-0.6334	0.2230
-0.6334	0.1907
-0.4574	0.2333
-0.3325	0.2383
0.0656	0.2178

Figure 5.4.3 Log (reaction rate) vs. log (2-butyne-1,4-diol concentration)

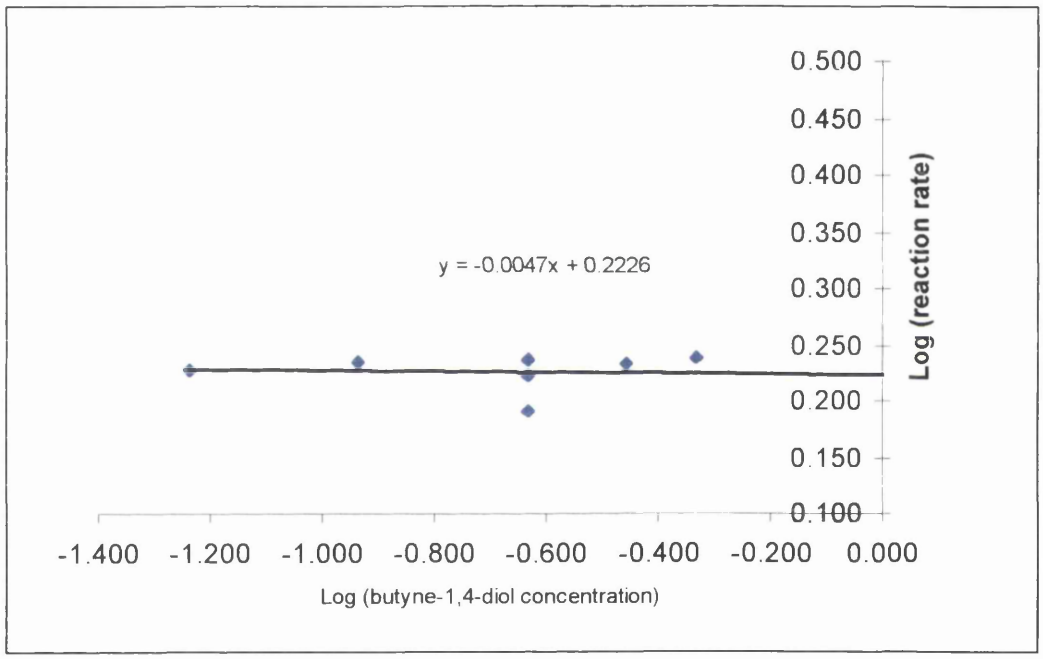


Table 5.4.4 Rate of 2-butyne-1,4-diol consumption vs. initial *cis*-2-butene-1,4-diol concentration at 338K over 0.2500g 1% Pd/C catalyst

Initial *cis*-2-butene-1,4-diol concentration (moles/l)	Rate of 2-butyne-1,4-diol consumption (moles x 10^{-5}/l/s/g catalyst)
0.0568	1.9612
0.1136	1.8125
0.2273	2.1245
0.2273	1.9423
0.2273	1.8812
0.3409	1.9214
0.4545	1.8321
1.1364	1.8821

Figure 5.4.4 Rate of 2-butyne-1,4-diol consumption vs. initial *cis*-2-butene-1,4-diol concentration at 338K over 0.2500g 1% Pd/C catalyst

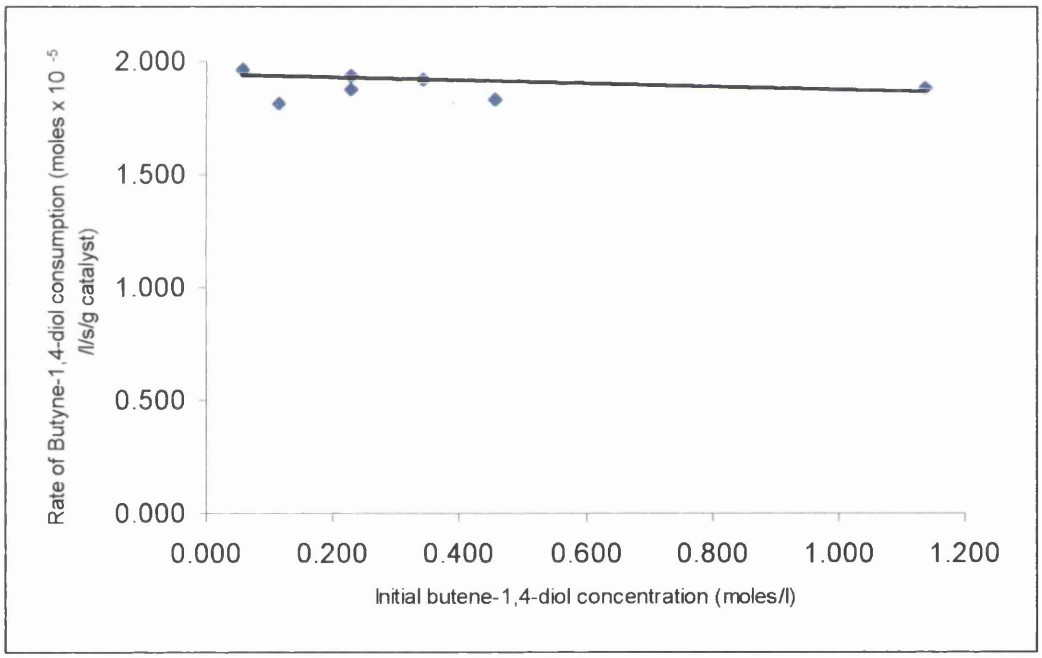
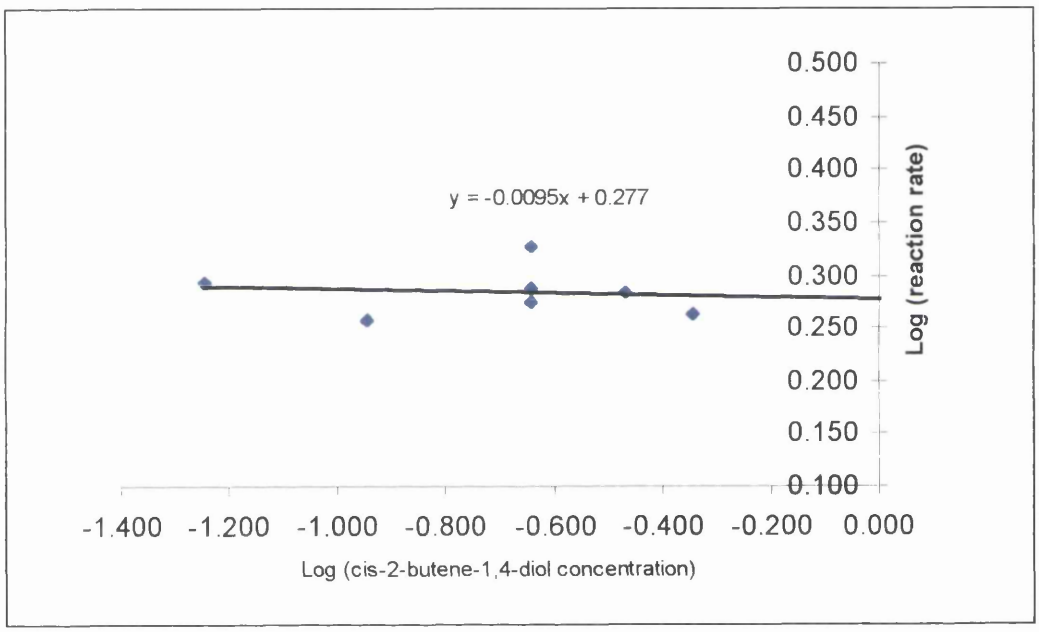


Table 5.4.5 Log (reaction rate) vs. log (*cis*-2-butene-1,4-diol concentration)

Log (*cis*-2-butene-1,4-diol concentration)	Log (reaction rate)
-1.2455	0.2925
-0.9445	0.2583
-0.6435	0.3273
-0.6435	0.2883
-0.6435	0.2744
-0.4674	0.2836
-0.3424	0.2629
0.0555	0.2746

Figure 5.5.3 Log (reaction rate) vs. log (*cis*-2-butene-1,4-diol concentration)



5.5 DETERMINATION OF ACTIVATION ENERGIES

This section outlines reactions that were conducted at ambient pressure to investigate the activation energies for the 1% Pd/C and the 1% Pd/Al_2O_3 (nitrate precursor) catalysts for the selective hydrogenation of 2-butyne-1,4-diol. The purpose of a catalyst is to reduce the activation energy of a reaction, E_a, when compared to that that would be expected for an equivalent uncatalysed process.

The selective hydrogenation of 2-butyne-1,4-diol has been studied with a number of catalysts. There are few published literature studies that investigate the activation energy for the hydrogenation of 2-butyne-1,4-diol. Fukuda and Kusama determined the activation energy for hydrogenation of 2-butyne-1,4-diol to be 21.71 kJ/mole when employing a $Pd/CaCO_3$ catalyst [24] in a glass reaction vessle. Later work by Chaudhari *et al* employing a $Pd\text{-}Zn/CaCO_3$ [21] and a Pd/C catalyst [22] found the activation energy for the hydrogenation of 2-butyne-1,4-diol to be 39.30 kJ/mole and 34.40 kJ/mole respectively. Both studies were carried out in a batch autoclave reactor. Telkar *et al* found the activation energy to 39.42 kJ/mole, employing a $Pd/CaCO_3$ catalyst [20] in a batch autoclave reactor.

To investigate the activation energies for the two catalysts the selective hydrogenation of 2-butyne-1,4-diol was conducted between 20 and 65^0C. The rate increases do not reach a maximum over the studied range of temperature for both of the catalysts. For each reaction k, the rate coefficient was calculated using the equation below:-

Equation 5.5.1

$$\ln\frac{(Ao)}{(At)}=kt$$

where k is the rate coefficient, A_o and A_t are the initial concentration of the reaction reagent and the concentration of the reaction reagent at time t, and t is time. By plotting $\ln(A_o/A_t)$ vs. t, the slope of the resulting straight line will be k.

When the rate constant k is known, an Arrhenius plot can be constructed and E_a determined using the equation:-

Equation 5.5.2

$$k = Ae^{-Ea/RT}$$

where k is the rate constant, A is the pre-exponential factor, E_a is the activation energy, R is the gas constant and T is the absolute temperature. By plotting ln k vs. 1/T, the slope of the resultant is $(-E_a/R)$. E_a can be obtained therefore by multiplying by (-R) to obtain E_a. Equations 5.5.1 and 5.5.2 are applicable when the overall reaction rate is first order.

Table 5.5.1 details the ln (k) and 1/T values for the activation energy reactions that were conducted with the 1% Pd/C catalyst, Figure 5.5.1 is the Arrhenius plot for the 1% Pd/C catalyst. Table 5.5.2 details the ln (k) and 1/T values for the activation energy reactions that were conducted with the 1% Pd/Al_2O_3 catalyst, Figure 5.5.2 is the Arrhenius plot for the 1% Pd/Al_2O_3 catalyst.

The activation energy for 2-butyne-1,4-diol hydrogenation employing the 1% Pd/C catalyst was found to be 37.1±1.4 kJ/mole. The activation energy for 2-butyne-1,4-diol hydrogenation employing the 1% Pd/Al_2O_3 catalyst was found to be 38.51 ±1.5 kJ/mole. The two activation energies are close to the values detailed in the literature for the more recent work [20, 21, 22]. As with the results from Sections 5.3 and 5.4 for the competitive adsorption and order of reaction studies respectively, the determined activation energies imply that the system is under kinetic control and not diffusion control [25b, 30].

Table 5.5.1 Ln (k) vs. 1/T for ambient pressure reaction vessel employing the 1% Pd/C catalyst

Temperature (K)	1/T	Ln (k)
298	0.00336	-12.614
308	0.00325	-12.006
308	0.00325	-11.988
313	0.00319	-11.721
318	0.00314	-11.505
323	0.00310	-11.310
328	0.00305	-11.145
328	0.00305	-11.091
338	0.00296	-10.770
338	0.00296	-10.809

Table 5.5.2 Ln (k) vs. 1/T for ambient pressure reaction vessel employing the 1% Pd/Al_2O_3 catalyst

Temperature (K)	1/T	Ln (k)
293	0.00341	-10.570
293	0.00341	-10.569
298	0.00336	-10.343
303	0.00330	-9.688
303	0.00330	-9.679
323	0.00310	-8.932
328	0.00305	-8.712
328	0.00305	-8.733
338	0.00296	-8.448
338	0.00296	-8.421

Figure 5.5.1 Arrhenius plot for the selective hydrogenation of 2-butyne-1,4-diol employing the 1% Pd/C catalyst

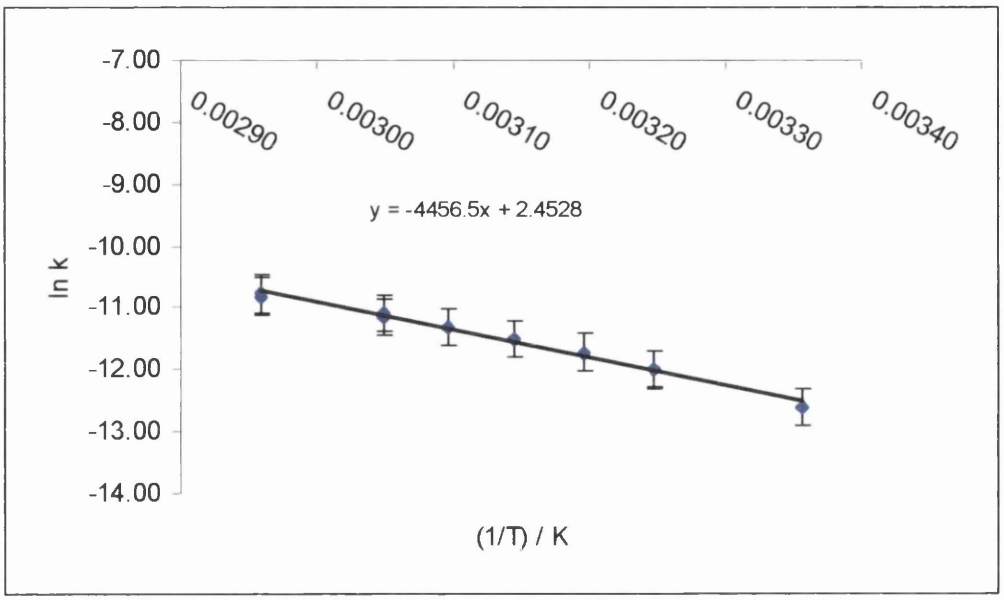
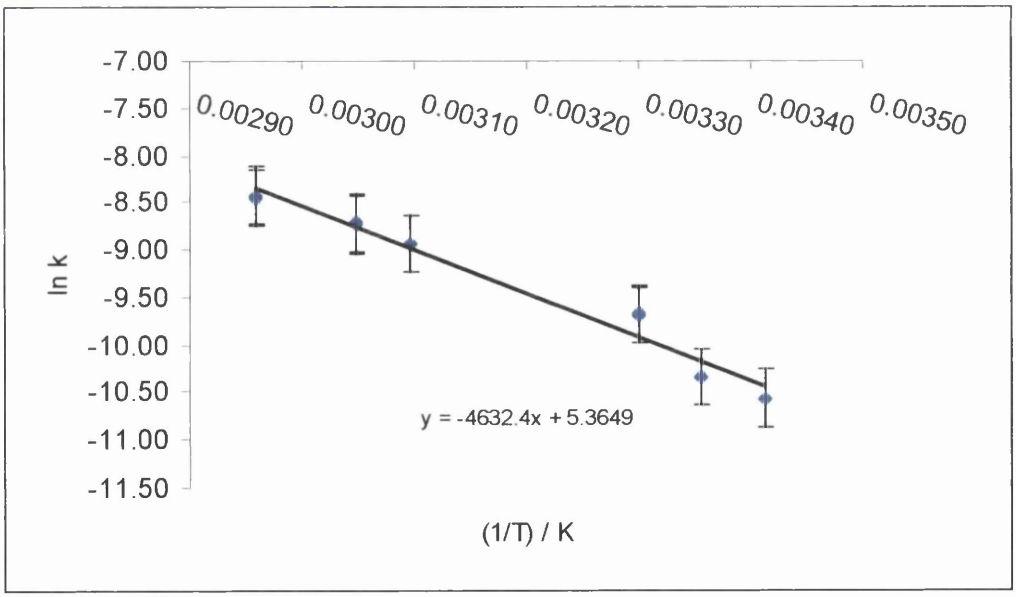


Figure 5.5.2 Arrhenius plot for the selective hydrogenation of 2-butyne-1,4-diol employing the 1% Pd/Al_2O_3 (nitrate precursor) catalyst



5.5.1 SUMMARY FOR SECTIONS 5.3, 5.4 AND 5.5

- Due to the fact 2-butyne-1,4-diol is more strongly adsorbed on the catalyst surface than *cis*-2-butene-1,4-diol, it is able to prevent any (significant) adsorption of *cis*-2-butene-1,4-diol, and hence retard any hydrogenation of *cis*-2-butene-1,4-diol while there is still 2-butyne-1,4-diol present in the reaction solution.

- Iso-propoxytetrahydrofuran, butane-1,4-diol, butanol, *cis* and *trans*-crotyl alcohol and 3-buten-1-ol come form *cis*-2-butene-1,4-diol, rather than directly from 2-butyne-1,4-diol. When 2-butyne-1,4-diol is present we see little production of these "side products" as in Figures 5.2.1 and 5.2.2.

- The activation energies for the hydrogenation of 2-butyne-1,4-diol was found to be 37.05 ±1.4 kJ/mole and 38.51 ±1.5 kJ/mole for the 1% Pd/C and the 1% Pd/Al_2O_3 (nitrate precursor) catalysts respectively.

- The rate of 2-butyne-1,4-diol hydrogenation varies linearly with catalyst mass, hence the reaction is first order with respect to catalyst mass.

- The initial concentration of 2-butyne-1,4-diol does not have any effect on the rate of 2-butyne-1,4-diol hydrogenation, hence the reaction is zero order with respect to 2-butyne-1,4-diol concentration.

- The initial concentration of *cis*-2-butene-1,4-diol does not have any effect on the rate of 2-butyne-1,4-diol hydrogenation, hence the reaction is zero order with respect to *cis*-2-butene-1,4-diol concentration.

- The ambient pressure reaction system is not diffusion limited and operates under kinetic control, this indicates the validity of the ambient pressure reaction vessel as a means of evaluating different catalysts.

5.6 CONTINUOUS ADDITION REACTIONS

This section summarises a number of reactions that were conducted using the continuous addition outlined in Section 3.6. The main focus of the discussion up to this point has concerned the selective hydrogenation of 2-butyne-1,4-diol to *cis*-2-butene-1,4-diol, using a single addition of 2-butyne-1,4-diol dissolved in propan-2-ol at the start of the reaction employing either the ambient or elevated pressure reaction vessels. With a vessel modified to allow for the continuous addition of reaction reagent throughout the experimental run. The reaction profile, concentrations of the products, and the selectivity to the formation of the observed reaction products may all be effected. The modified reaction vessel that was employed for the experiments that were conducted for this section allowed for a constant flow of a known concentration of 2-butyne-1,4-diol to be introduced into the reaction vessel over the course of the experimental runs. With the constant replenishment of the 2-butynel-4-diol during the course of the experiments, the concentration of 2-butyne-1,4-diol was kept in excess of the *cis*-2-butene-1,4-diol concentration for a considerable amount of reaction time. Even when the 2-butyne-1,4-diol is not in excess the of the *cis*-2-butene-1,4-diol, there is enough 2-butyne-1,4-diol present in the reaction vessel to severely retard the formation of the other "side products".

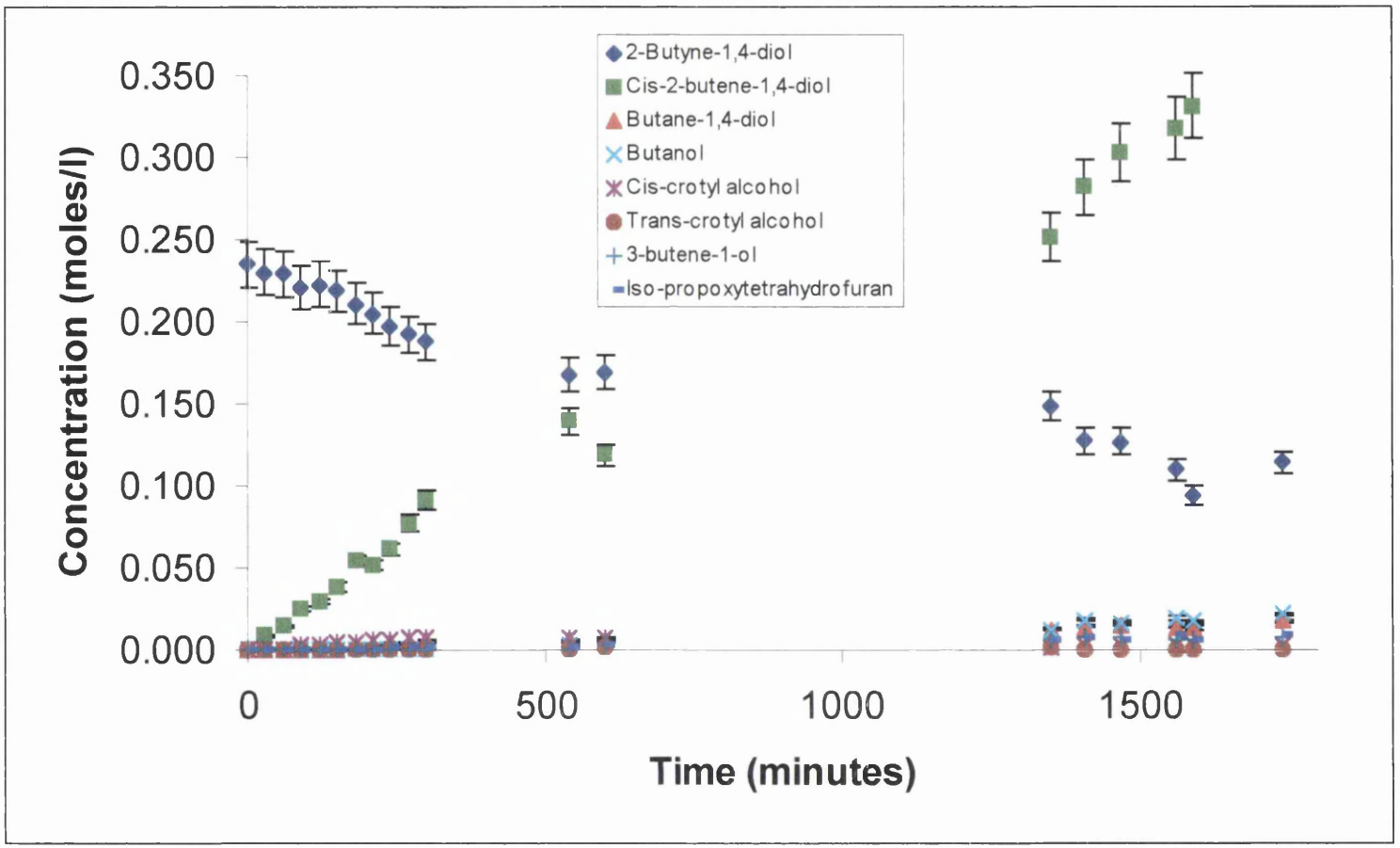
The purpose of the section is not to examine continuous stirred tank reactor type regime [31] but to investigate a set of reaction parameters where the 2-butyne-1,4-diol concentration is tried to be maintained at its initial concentration throughout the course of the reaction. With an overflow and recycling line the reactor that was used for the experiments detailed in this section could be modified to operate in a continuous stirred tank reactor type manner. This maybe considered future work, and as such is not discussed in this section.

Table 5.6.1 details a summary of the reaction data, and Figure 5.6.1 shows a reaction profile for ambient pressure reactions employing the 1% Pd/C catalyst with 2-butyne-1,4-diol and the reaction vessel modified to accept continuous addition of a reaction reagent solution. The experimental procedure for Figure 5.6.1 was the same as that detailed in Section 3.7 for an ambient pressure reaction that employed a programmed reduction of the catalyst with the modified ambient reaction vessel. The selectivity throughout the reaction was reduced to around 80%, instead of around 95% as see in Figure 5.2.1. There was also the suppression of "side products". This was due to the presence of 2-butyne-1,4-diol in the reaction vessel that inhibited the formation of the "side products" from *cis*-2-butene-1,4-diol.

Table 5.6.1 Continuous addition reaction employing the 1% Pd/C catalyst

Time (minutes)	Butyne-1,4-diol (moles/l)	Butene-1,4-diol (moles/l)	Butane-1,4-diol (moles/l)	Butanol (moles/l)	*Cis*-crotyl alcohol (moles/l)	*T*-crotyl alcohol (moles/l)	3-butene-1-ol (moles/l)	Iso-propoxythf (moles/l)	Conversion (%)	Selectivity (%)
0	0.2151	0	0	0	0	0	0	0	0	0
30	0.2293	0.0052	0	0	0	0	0	0	4.69	72.57
60	0.2289	0.0123	0	0	0	0	0	0	7.37	78.57
90	0.2145	0.0212	0	0	0.0034	0	0	0	12.68	77.88
120	0.2727	0.0351	0	0	0.0035	0	0	0	14.05	79.95
150	0.1784	0.0332	0	0	0.0045	0	0	0	17.62	81.80
180	0.1771	0.0362	0.0012	0	0.0048	0	0	0	22.17	90.18
210	0.1653	0.0421	0.0032	0	0.0059	0	0	0	26.02	70.87
240	0.2221	0.0672	0.0037	0	0.0062	0	0	0.0009	30.24	71.50
270	0.2284	0.0812	0.0039	0	0.0079	0	0	0.0010	33.55	79.59
300	0.1876	0.0735	0.0052	0	0.0067	0	0	0.0012	36.43	85.12
540	0.1543	0.0692	0.0053	0.0023	0.0069	0	0	0.0021	51.24	79.18
600	0.1542	0.0884	0.0049	0.0067	0.0078	0.0012	0.0027	0.0023	52.35	63.69
1350	0.1081	0.2516	0.0123	0.0121	0.0021	0.0009	0.0056	0.0058	70.68	70.48
1410	0.1273	0.2721	0.0139	0.0182	0.0035	0	0.0078	0.0067	75.38	72.37
1470	0.1271	0.2829	0.0152	0.0162	0.0029	0	0.0069	0.0065	75.98	75.35
1560	0.1096	0.2672	0.0139	0.0192	0.0034	0	0.0062	0.0081	79.97	72.50
1590	0.0941	0.2413	0.0132	0.0173	0.0034	0	0.0064	0.0059	82.99	72.18
1740	0.1142	0.3251	0.0171	0.0214	0.0032	0	0.0071	0.0091	80.42	82.13

Figure 5.6.1 Reaction profile for continuous addition reaction employing the 1% Pd/C catalyst



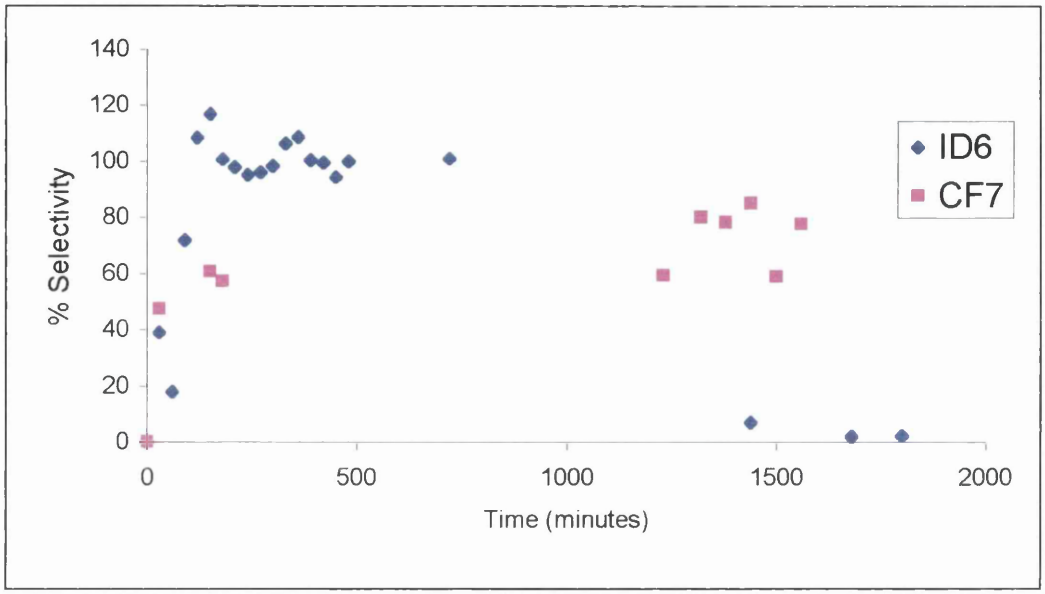
5.6.1 Discussion for continuous addition reactions

In the reaction detailed in this section 2-butyne-1,4-diol was delivered linearly into the reactor vessel, employing the syringe pump. However, the 2-butyne-1,4-diol does not remain at a fixed concentration, as was initially intended when the continuous addition experiments were first conducted (2-butyne-1,4-diol is decreasing in concentration within the vessel). The problem with the syringe pump was it was difficult to match the amount of 2-butyne-1,4-diol that was introduced into the reaction vessel during the course of the experiment with the activity of the catalyst. This explains the slope in the 2-butyne-,4-diol concentration that is observed in Figure 5.6.1.

The concentration of *cis*-2-butene-1,4-diol increased linearly during the course of Figure 5.6.1. 2-butyne-1,4-diol and *cis*-2-butene-1,4-diol crossover after approximately 700 minutes. However, as long as the 2-butyne-1,4-diol is in excess (or present in the reaction vessel), the *cis*-2-butene-1,4-diol cannot undergo significant reaction on the catalyst surface and, hence, the concentration of "side products" is suppressed. Similar observations, for the same reasons were made in Section 5.3 for the competitive addition experiments.

Unlike the ambient and elevated pressure reactions in Section 5.2 the major product in the later stage of the reaction in Figure 5.6.1 was *cis*-2-butene-1,4-diol rather than iso-propoxytetrahydrofuran. This suggests a change in selectivity with respect to the reaction mechanism. For Figure 5.6.1 the selectivity levels out at approximately 80% after the initial stage of the continuous addition reaction, this is considerably lower than the 95% selectivity to cis-2-butene-1,4-diol formation that was observed in the reaction in Section 5.2 (Figure 5.2.1). Unlike in Figure 5.2.1, in Figure 5.6.1 there was more *cis*-crotyl alcohol produced than *trans*-crotyl alcohol, this may have to do with the increased residence time a surface bound intermediate has so that *cis*-crotyl alcohol is formed rather than *trans*-crotyl alcohol.

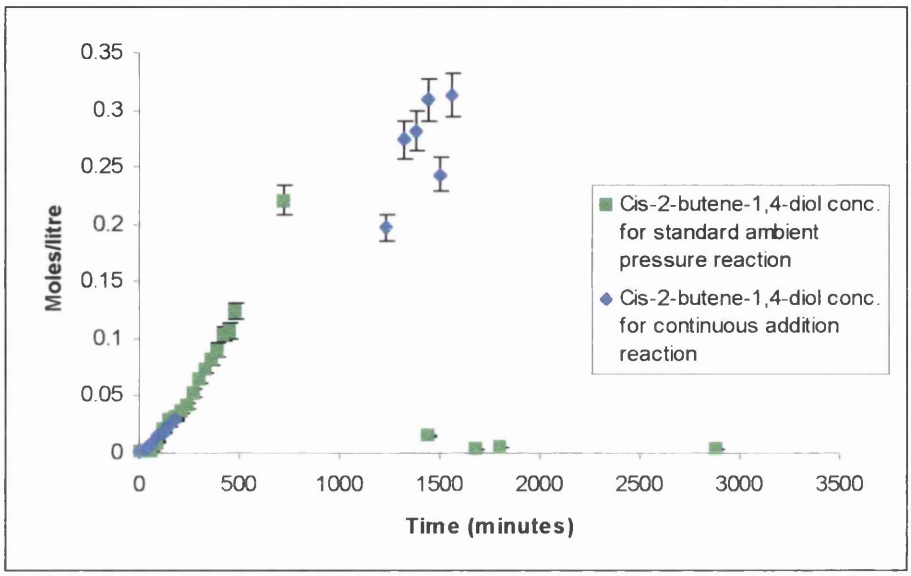
Figure 5.6.2: Comparison of selectivity to *cis*-2-butene-1,4-diol formation for a standard ambient pressure reaction and a continuous addition reaction



For the standard ambient pressure reaction (ID6, represented here by the blue diamonds) there is a selectivity towards *cis*-2-butene-1,4-diol formation of approximately 95% during the hydrogenation of 2-butyne-1,4-diol. When *cis*-2-butene-1,4-diol undergoes subsequent hydrogenation, this selectivity then drops to zero. For the continuous addition reaction (CF7, represented here by the purple squares) there is a constant selectivity towards *cis*-2-butene-1,4-diol of approximately 80%. This is not as high as that obtained in the standard ambient pressure reactor, but the catalyst is working at constant conversion of 2-butyne-1,4-diol, and this leads to a constant linear increase of *cis*-2-butene-1,4-diol concentration, *cis*-2-butene-1,4-diol is being produced at a constant rate.

Another way to consider the differences between continuous operation of the reactor and a reactor operating under batch mode is to consider Figure 5.6.3 below. Figure 5.6.3 compares the amount of *cis*-2-butene-1,4-diol produced throughout the reaction for both the standard ambient and continuous modes of operation.

Figure 5.6.3: Comparison of *cis*-2-butene-1,4-diol production for a standard ambient pressure reaction and a continuous addition reaction



The main advantage that the continuous addition reactor has over the unmodified ambient pressure reaction vessel is that *cis*-2-butene-1,4-diol is produced throughout the whole of the reaction in the continuous reaction (Figure 5.6.1), but not throughout the whole reaction when the unmodified ambient pressure reaction vessel is employed (*e.g.* Figure 5.2.1). Once all the 2-butyne-1,4-diol has been hydrogenated in Figure 5.2.1 the *cis*-2-butene-1,4-diol can be hydrogenated. In the continuous reaction however (Figure 5.6.1), it is possible to continue the production of *cis*-2-butene-1,4-diol for as long as 2-butyne-1,4-diol is added to the system. It would be feasible to run the continuous process on a large scale, providing that all the unwanted by-products could be successfully separated.

5.6.2 SUMMARY FOR SECTION 5.6

- It was difficult to match the catalyst activity with the flow of reagent solution from the syringe pump.

- More *cis*-crotyl alcohol was formed than *trans*-crotyl alcohol in Figure 5.6.1, this is the opposite of what was observed in Figure 5.2.1. The selectivity at the catalyst surface has changed.

- There was effectively no mass inbalance observed in Figure 5.6.1.

- *Cis*-2-butene production with the suppression of "side products", will continue as long as there is 2-butyne-1,4-diol in the reaction vessel.

5.7 OTHER 1% SUPPORTED PALLADIUM CATALYSTS

This section summarises reactions that were conducted at ambient pressure reaction using two 1% Pd/Al_2O_3 catalysts, one derived from $PdCl_2$ and the other derived form $Pd(NO_3)_2$. The two catalysts were prepared in-house, their preparation is detailed in the experimental chapter.

The main focus of this project up to this point has concerned the selective hydrogenation of 2-butyne-1,4-diol to *cis*-2-butene-1,4-diol using the 1% Pd/C catalyst as supplied by ICI Synetix. The other 1% supported palladium catalysts were prepared to estimate the sensitivity of the chemistry observed with other supported palladium catalysts. The characterisation of the palladium catalysts is discussed in Section 5.1. Tables 5.7.1 and 5.7.2 detail a summary of the reaction data, and Figures 5.7.1 and 5.7.2 show reaction profiles for ambient pressure reactions employing the 1% Pd/Al_2O_3 (chloride precursor) and 1% Pd/Al_2O_3 (nitrate precursor) catalysts respectively.

The experimental procedure for these experiments was the same as that detailed in Section 3.5 for an ambient pressure reaction with programmed reduction of the catalyst. The only difference was the use if the 1% Pd/Al_2O_3 (chloride precursor, Figure 5.7.1) and the 1% Pd/Al_2O_3 (nitrate precursor, Figure 5.7.1) catalysts respectively, instead of the 1% Pd/C catalyst. Thus a conversion of the 2-butyne-1,4-diol of 91.06% in 200 minutes, and 95.68% in 110 minutes was achieved with the 1% Pd/Al_2O_3 (chloride precursor) and the 1% Pd/Al_2O_3 (nitrate precursor) catalysts respectively. The rate of 2-butyne-1,4-diol hydrogenation for Figures 5.7.1 and 5.7.2 was 6.68×10^{-5} and 1.30×10^{-4} moles/l/s/g catalyst respectively. A selectivity in the order of 90% towards the formation of *cis*-2-butene-1,4-diol was maintained up to 91.06% conversion and 95.68% conversion for the 1% Pd/Al_2O_3 (chloride precursor) catalyst and the 1% Pd/Al_2O_3 (nitrate precursor) catalyst respectively.

As with the ambient pressure reactions that employed the 1% Pd/C catalyst for the hydrogenation of 2-butyne-1,4-diol (Section 5.2) there was formation of

iso-propoxytetrahydrofuran observed during the course of the reaction for both of the experiments detailed in this section. With the 1% Pd/Al_2O_3 (chloride precursor) catalyst an additional compound, 2-butyne-1-ol (identified by GC-MS and ^1H NMR analysis) was also formed that had not been observed in the previous reactions that used the 1% Pd/C catalyst. With the 1% Pd/Al_2O_3 (nitrate precursor) catalyst there was also the formation of an additional compound, hydroxy-tetrahydrofuran (identified by GC-MS and ^1H NMR analysis) that had not been observed in the previous reactions that used the 1% Pd/C catalyst. Full hydrogenation of 2-butyne-1,4-diol was effectively reached in 200 and 110 minutes for the chloride and nitrate precursor catalysts respectively. This compares favourably with the time it took to reach full hydrogenation of 2-butyne-1,4-diol with the 1% Pd/C catalyst (Figure 5.2.1), with it requiring 720 minutes to fully hydrogenate 2-butyne-1,4-diol.

The mass balance at the end of the reaction for both of these experiments was 95.96 and 94.94% for the 1% Pd/Al_2O_3 (chloride precursor, Figure 5.7.3a)) and (nitrate precursor, Figure 5.7.3b)) respectively, the mass balance for both of the reactions being effectively complete. By comparison, the mass balance for Figure 5.2.1(Figure 5.7.3 c)) was 70.61%.

Table 5.7.1 Ambient pressure reaction employing the 1% Pd/Al_2O_3 (chloride precursor) catalyst

Time (minutes)	Butyne-1,4-diol (moles/l)	Butene-1,4-diol (moles/l)	Butane-1,4-diol (moles/l)	Butanol (moles/l)	*Cis*-crotyl alcohol (moles/l)	*Trans*-crotyl alcohol	3-butene-1-ol (moles/l)	Iso-propoxythf (moles/l)	2-butyne-1-ol (moles/l)	Conversion (%)	Selectivity (%)
0	0.2371	0	0	0	0	0	0	0	0	0	0
20	0.2113	0.0071	0	0	0.0023	0.0039	0	0	0	10.88	27.52
40	0.2161	0.0178	0.0031	0	0.0035	0.0045	0	0	0.0036	8.86	84.76
60	0.2015	0.0323	0.0040	0	0.0035	0.0052	0.0039	0.0010	0.0041	15.02	90.73
80	0.1836	0.0414	0.0042	0	0.0038	0.0060	0.0040	0.0017	0.0044	22.56	77.38
100	0.1692	0.0608	0.0042	0	0.0040	0.0072	0.0042	0.0028	0.0051	28.64	89.54
120	0.1383	0.0912	0.0043	0	0.0042	0.0090	0.0045	0.0037	0.0057	41.67	92.31
140	0.1182	0.1093	0.0049	0.0011	0.0043	0.0096	0.0048	0.0043	0.0061	50.15	91.93
160	0.1058	0.1180	0.0051	0.0014	0.0045	0.0108	0.0050	0.0048	0.0062	55.38	89.87
180	0.0662	0.1551	0.0070	0.0027	0.0047	0.0134	0.0055	0.0064	0.0025	72.08	90.76
200	0.0212	0.2032	0.0079	0.0040	0.0054	0.0183	0.0064	0.0092	0.0046	91.06	94.12
300	0.0091	0.0913	0.0092	0.0002	0.0204	0.0163	0.0093	0.0141	0.0025	96.16	40.04
1320	0.0007	0.0031	0.0261	0.0703	0.0136	0.0053	0.0045	0.1128	0.0025	99.71	1.31
1380	0.0007	0.0020	0.0233	0.0628	0.0125	0.0051	0.0041	0.1131	0.0025	99.71	0.85
1440	0.0007	0.0112	0.0220	0.0655	0.0131	0.0051	0.0041	0.1033	0.0025	99.71	4.74

Figure 5.7.1 Reaction profile for an ambient pressure reaction employing the 1% Pd/Al_2O_3 (chloride precursor) catalyst

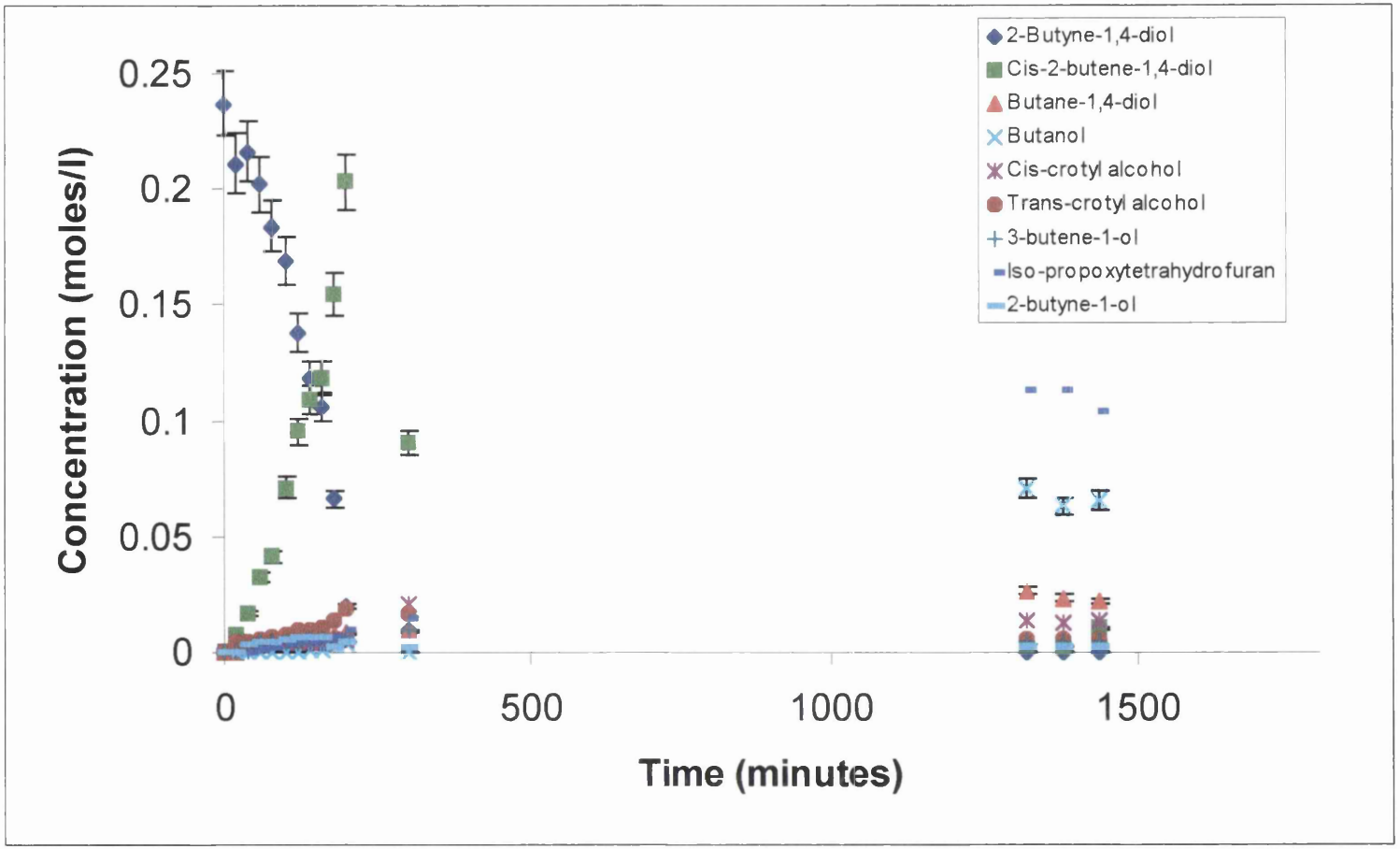


Table 5.7.2 Ambient pressure reaction employing the 1% Pd/Al_2O_3 (nitrate precursor) catalyst

Time (minutes)	Butyne-1,4-diol (moles/l)	Butene-1,4-diol (moles/l)	Butane-1,4-diol (moles/l)	Butanol (moles/l)	*Cis*-crotyl alcohol (moles/l)	*T*-crotyl alcohol (moles/l)	3-butene-1-ol (moles/l)	Iso-propoxythf (moles/l)	Hydroxy-thf (moles/l)	Conversion (%)	Selectivity (%)
0	0.2262	0	0	0	0	0	0	0	0	0	0
10	0.2168	0.0073	0	0	0	0	0	0.0010	0	4.16	77.96
20	0.1892	0.0195	0	0	0	0	0	0.0016	0	16.36	52.74
30	0.1816	0.0321	0	0	0	0	0	0.0014	0	19.72	72.02
40	0.1453	0.0405	0	0	0	0	0	0.0019	0	35.78	50.00
50	0.1321	0.0559	0	0	0	0	0	0.0018	0	41.60	59.46
60	0.1397	0.0894	0	0	0	0.0021	0	0.0014	0	38.27	103.29
70	0.1073	0.1097	0	0	0	0.0038	0.0015	0.0017	0	52.56	92.29
80	0.0719	0.1369	0	0	0	0.0042	0.0027	0.0018	0.0027	68.21	88.71
90	0.0485	0.1521	0.0029	0	0	0.0044	0.0037	0.0016	0.0031	78.55	85.59
100	0.0296	0.1805	0.0030	0	0.0015	0.0047	0.0038	0.0015	0.0034	86.91	91.77
110	0.0098	0.1910	0.0064	0	0.0029	0.0051	0.0043	0.0015	0.0071	95.68	88.22
120	0.0085	0.1592	0.0091	0	0.0039	0.0048	0.0048	0.0014	0.0085	96.25	73.09
130	0.0078	0.1311	0.0193	0	0.0040	0.0056	0.0038	0.0015	0.0247	96.55	60.02
140	0.0077	0.1042	0.0265	0	0.0041	0.0052	0.0037	0.0016	0.0501	96.62	47.66
150	0.0076	0.0899	0.0574	0.0004	0.0043	0.0050	0.0039	0.0017	0.0808	96.63	41.14
160	0.0075	0.0536	0.0478	0.0010	0.0047	0.0052	0.0038	0.0013	0.0901	96.69	24.50
170	0.0075	0.0393	0.0446	0.0063	0.0050	0.0050	0.0036	0.0270	0.0808	96.71	17.95
180	0.0073	0.0167	0.0468	0.0075	0.0050	0.0048	0.0065	0.0473	0.0690	96.77	7.65
210	0.0072	0.0012	0.0603	0.0081	0.0066	0.0051	0.0071	0.0972	0.0276	96.81	0.56
400	0.0072	0.0012	0.0638	0.0092	0.0068	0.0052	0.0074	0.1092	0.0047	96.83	0.55

Figure 5.7.2 Reaction profile for ambient pressure reaction employing the 1% Pd/Al_2O_3 (nitrate precursor) catalyst

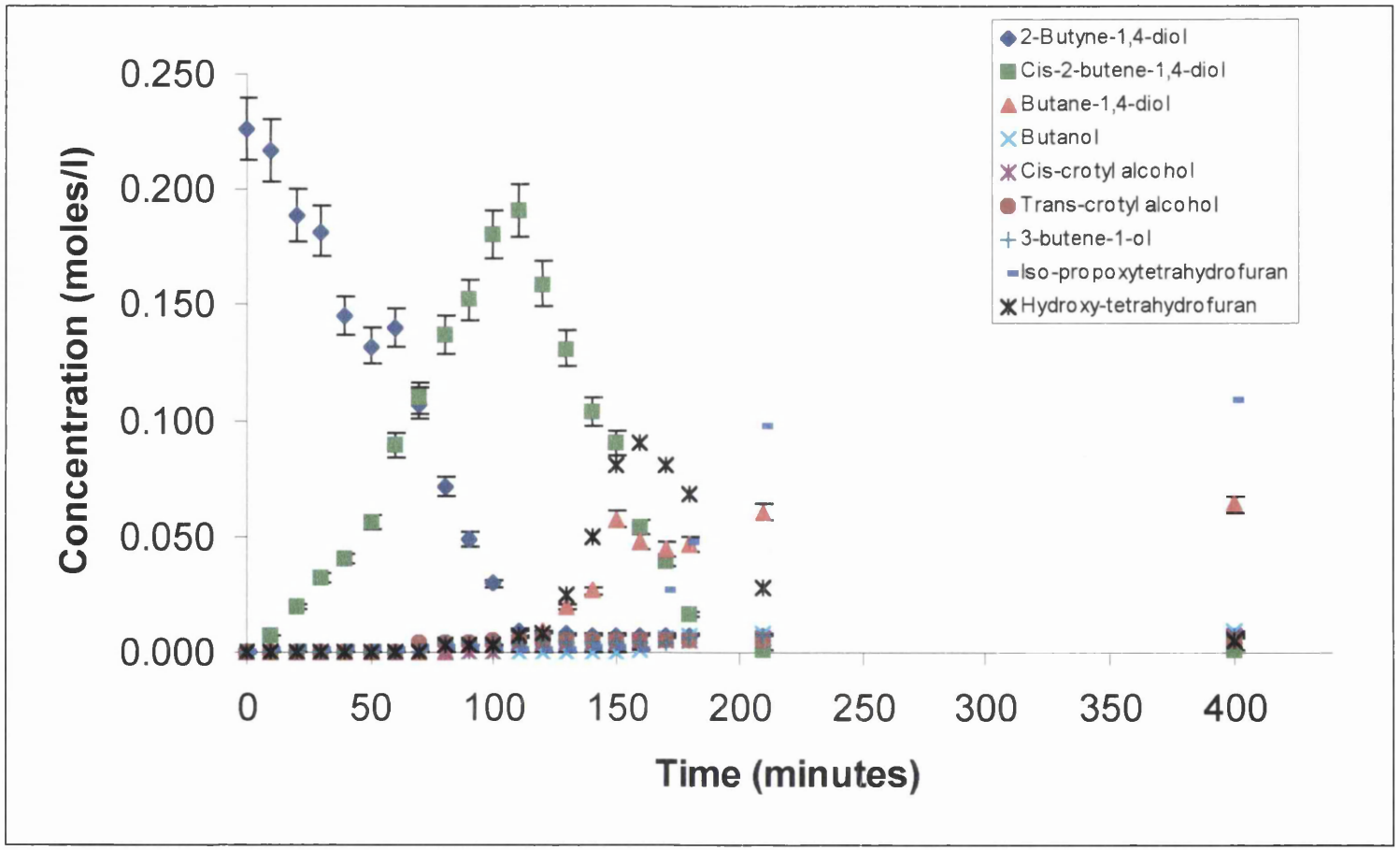
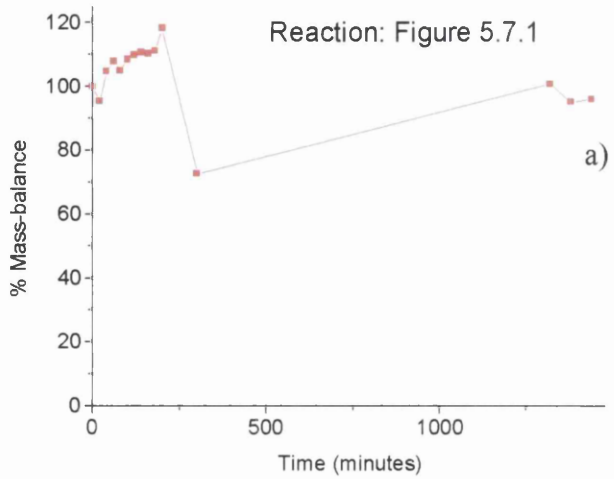


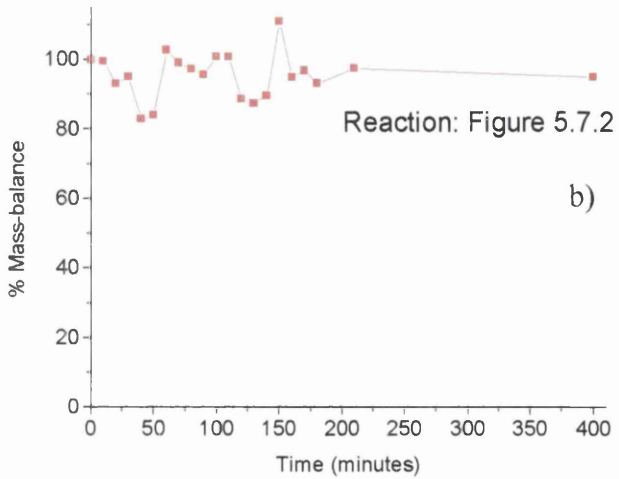
Table 5.7.3 Comparative summary for Section 5.7 and Section 5.2 (Figure 5.2.1)

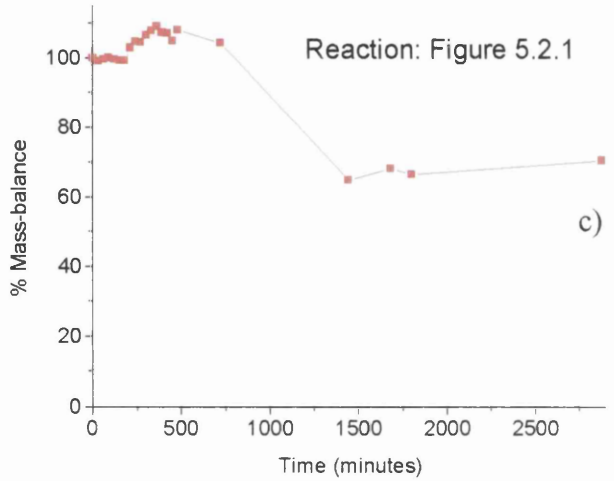
Catalyst	Rate of reaction (moles/l/s/g catalyst)	Pd surface/g catalyst	% Dispersion	Ave. particle size (nm)	T.O.F (moles/l/s/ Pd surface)
1% Pd/C	1.96×10^{-5}	5.41×10^{18}	9.56	11.40	3.62×10^{-24}
1% Pd/Al_2O_3 (nitrate precursor)	1.30×10^{-4}	5.34×10^{19}	94.41	1.15	2.43×10^{-24}
1% Pd/Al_2O_3 (chloride precursor)	6.68×10^{-5}	3.29×10^{19}	70.01	1.56	2.03×10^{-24}

Catalyst	Final product order	Final % mass balance	% Conversion at time=100 minutes
1% Pd/C	Iso-propoxythf, butane-1,4-diol, butanol and *cis*-crotyl alcohol	70.61	9.63
1% Pd/Al_2O_3 (nitrate precursor)	Iso-propoxythf, butanediol, butanol and 3-butene-1-ol	94.94	86.91
1% Pd/Al_2O_3 (chloride precursor)	Iso-propoxythf, butanol, butane-1,4-diol and *cis*-crotyl alcohol	95.96	28.63

Figure 5.7.3 Mass-balances for reactions from Section 5.7 and Figure 5.2.1 from Section 5.2







5.7.1 Discussion for other 1% supported palladium catalysts

Table 5.7.3 details summary data for the 1% Pd/C, 1% Pd/Al_2O_3 (chloride precursor) 1% Pd/Al_2O_3 (nitrate precursor) catalysts. The catalysts detailed in this section have increased rates of hydrogenation of 2-butyne-1,4-diol when compared to the 1% Pd/C catalyst. The rate of hydrogenation for the 1% Pd/Al_2O_3 (chloride precursor) 1% Pd/Al_2O_3 (nitrate precursor) catalysts are around 3.4 and 6.6 times faster respectively. These increased rates can be accounted for by the greatly increased dispersion for the catalysts employed in this section, leading to surface palladium/g of the catalysts being 9.87 and 6.08 times greater than that for the 1% Pd/C catalyst for the chloride and nitrate derived precursor catalysts. The T.O.F. values for all three catalysts are within the same order of magnitude, despite the increased surface palladium for the two 1% Pd/Al_2O_3 catalysts, therefore increased surface palladium available for hydrogenation would be expected to lead to an increase in the reaction rate. The increased rate is also reflected in the amounts of conversion at 100 minutes into the reaction on for the different supported palladium catalysts in Table 5.7.3. The 1% Pd/Al_2O_3 (nitrate precursor) has the greatest extent of conversion followed by the 1% Pd/Al_2O_3 (chloride precursor), then the 1% Pd/C catalyst.

Table 5.7.3 shows that not only are the final product distributions for the two 1% Pd/Al_2O_3 catalysts different from each other, but also different form the final product distribution for the selective hydrogenation of 2-butyne-1,4-diol employing the 1% Pd/C catalyst (Figure 5.2.1).When the 1% Pd/C catalyst was employed the product that was produced in the highest concentration by the end of the reaction was iso-propoxytetrahydrofuran followed by butane-1,4-diol, butanol and *cis*-crotyl alcohol. For the 1% Pd/Al_2O_3 (chloride precursor) catalyst the order was iso-propoxytetrahydrofuran followed by butanol and 3-buten-1-ol. For the 1% Pd/Al_2O_3 (nitrate precursor) catalyst the order was iso-propoxytetrahydrofuran followed by butanol, butane-1,4-diol and *cis*-crotyl alcohol.

The relative concentrations of the products also varied from catalyst to catalyst. When the 1% Pd/C catalyst the final concentration of butanol was in the order of 0.0309M (Figure 5.2.1). In the reactions in this section the final concentration of butanol was 0.0655M for the chloride derived catalyst and 0.0092M for the nitrate derived catalyst. The final butane-1,4-diol concentration when the 1% Pd/C catalyst was employed was 0.0432M, for this reactions in this section the final concentration of butane-1,4-diol was 0.0220M for the chloride derived catalyst and 0.0655M for the nitrate derived catalyst. There were also reduced amounts of *cis* and *trans*-crotyl alcohol and 3-buten-1-ol when the final product distributions for the reactions in this section are compared with the reactions with Figure 5.2.1. Another important difference between the reactions in this section and Figure 5.2.1 was the amount of iso-propoxytetrahydrofuran that was produced. In the reactions in this section the final concentration of iso-propoxytetrahydrofuran was 0.1033M for the chloride derived catalyst and 0.1092M for the nitrate derived catalyst as opposed to 0.0490M for the equivalent reaction that employs the 1% Pd/C catalyst (Figure 5.2.1).

Both the catalysts employed in this section have a product that is not observed when the 1% Pd/C catalyst was employed with previous reactions, with propan-2-ol as the reaction solvent. 2-butyne-1-ol was produced when the 1% Pd/Al_2O_3 (chloride precursor) catalyst was employed. This can be explained by considering a half hydrogenated 2-butyne-1,4-diol species adsorbed on the catalyst loosing a hydroxyl group and gaining a hydrogen atom, and desorbing to form 2-butyne-1-ol. The 1% Pd/Al_2O_3 (nitrate precursor) catalyst produces hydroxy-tetrahydrofuran during the course of the reaction, which is subsequently (largely) converted to iso-propoxytetrahydrofuran by the end of the reaction. The hydroxy-tetrahydrofuran forms from an interaction between the adsorbed intermediate species 3 that usually directly forms iso-propoxyterahydrofuran and the hydroxyl groups on the catalyst support. After desorbing from the catalyst the hydroxy-tetrahydrofuran is free to re-adsorb and go onto form iso-propoxytetrahydrofuran. These aspects of the reaction mechanism are discussed in more detail in Chapter 6.

If we consider the mass balance plots for the 1% Pd/Al_2O_3 (chloride precursor) catalyst, (Figure 5.7.3 a), 1% Pd/Al_2O_3 (nitrate precursor) catalyst, (Figure 5.7.3 b), and the 1% Pd/C catalyst (Figure 5.7.3 c) we can see that the mass balance profile for the catalysts employed in this section differ significantly. The mass balance for the 1% Pd/C catalyst collapses after all the 2-butyne-1,4-diol has been hydrogenated (720 minutes). This collapse is not due to *cis*-2-butene-1,4-diol being converted to the "side products", but due to there being significant amounts of butane and butene being produced from reaction intermediates that can account for the mass in-balance (the final mass balance was 70.61%). The mass balance for the reactions in this section are effectively complete, 95.96 and 94.94% for the 1% Pd/Al_2O_3 (chloride precursor) and 1% Pd/Al_2O_3 (nitrate precursor) respectively. The main difference between the catalysts that were employed for this section with the 1% Pd/C catalyst is the smaller metal particle size and increased dispersion.

The increased dispersion can account for the increased reaction rate experienced when employing the 1% Pd/Al_2O_3 catalysts. The smaller metal particles seem to enhance the rate coefficient for the production of the final reaction products. Iso-propoxytetrahydrofuran formation for both of the reaction detailed in this section was enhanced when compared to that observed when the 1% Pd/C catalyst was employed. The smaller metal particles seem to inhibit the formation of butene and butane that leads to a mass-imbalance when the 1% Pd/C catalyst was employed (*i.e.* larger metal particles are required for the formation of butene and butane from the reaction intermediates). Further discussion about this can be found in Chapter 6.

The two 1% Pd/Al_2O_3 catalysts detailed in this section show significantly different overall reaction profiles in terms of rate of hydrogenation and final product distribution to the reactions that employ 1% Pd/C catalyst detailed in Section 5.2. The selectivities towards *cis*-2-butene-1,4-diol formation for the catalysts in this section are in the order of 90%, lower than the 95% selectivity towards *cis*-2-butene-1,4-diol observed with the 1% Pd/C catalyst (Figure 5.2.1). With slightly different products, whether it is the presence of 2-butyne-1-ol in the chloride precursor derived catalyst experiment or the formation and

subsequent conversion of the hydroxy-tetrahydrofuran to iso-propoxytetrahydrofuran in the nitrate precursor derived catalyst experiment.

The catalyst derived form the nitrate precursor has a higher selectivity towards iso-propoxytetrahydrofuran and butane-1,4-diol formation than any of the other 1% palladium catalysts. The 1% Pd/Al_2O_3 (nitrate precursor) catalyst is the catalyst of choice if you wish to produce iso-propoxytetrahydrofuran at high yields, with reduced amounts of "side products" and considerably more rapidly than with the 1% Pd/C catalyst. Future work could look at changing the reaction solvent to see if other substituted furans could be produced from similar solvent/intermediate interactions.

5.7.2 SUMMARY FOR SECTION 5.7

- The rate of hydrogenation for the 1% supported palladium/alumina catalysts are approximately 3.4 times faster for the 1% Pd/Al_2O_3 (chloride precursor) and 6.6 times faster for the 1% Pd/Al_2O_3 (nitrate precursor) than for the 1% Pd/C catalyst.

- There are different final product distributions for the two 1% Pd/Al_2O_3 catalysts when compared with the 1% Pd/C catalyst.

- The mass-imbalance observed when the 1% Pd/C catalyst was employed (e.g. Figure 5.2.1) is not observed with the two 1% Pd/Al_2O_3 catalysts (with their mass-balances being effectively complete). The reaction pathway towards the formation of butane and butene are significantly retarded when the 1% Pd/Al_2O_3 catalysts are employed.

- Approximately double the amount of iso-propoxytetrahydrofuran was produced with both the 1% Pd/Al_2O_3 catalysts, than was produced when the 1% Pd/C catalyst was employed.

- The mass-balances for all the reactions in this section that employed the 1% Pd/Al_2O_3 catalysts were more complete than the mass-balances in Section 5.2. This suggests that the formation of butane and butene is less favourable when a mono-substituted alkyne or alkene is employed as the reaction reagent.

5.8 MONO-SUBSITUTED ALKYNES AND 3-BUTEN-1-OL

This section details a number of reactions that were conducted using mono-substituted alkynes and 3-buten-1-ol. The main focus of the discussion up to this point has concerned the selective hydrogenation of 2-butyne-1,4-diol to *cis*-2-butene-1,4-diol. There are however, a number of mono-substituted alkynes and alkenes formed in the various reactions that employ the palladium catalysts. In order to gain an increased understanding of how these products are formed, and the impact that they have on the overall reaction processes, reactions that employ mono-substituted alkynes and 3-buten-1-ol have been undertaken. The reactions in this section also set out to examine if ti is possible to form iso-propoxytetrahydrofuran using mono-substituted alkynes and 3-buten-1-ol. The reactions up to this point in Sections 5.2, 5.3 and 5.6 have only employed 2-butyne-1,4-diol and *cis*-2-butene-1,4-diol as their reaction reagent. It may not be possible to form iso-propoxytetrahydrofuran without the presence of the diol functionality in the reaction reagent.

The possible interaction between 3-butene-1-ol, *cis* and *trans* crotyl alcohol can be investigated using a range of mono-substituted alcohols. Experiments described up to this point have illustrated the possibility that there can isomerisation between the *cis* and *trans* forms of crotyl alcohol and 3-buten-1-ol (Sections 5.2, 5.3 and 5.6). Mono-substituted alkynes that can be hydrogenated to form either the *cis* or *trans*-crotyl alcohol, or can be hydrogenated to form 3-buten-ol, can give us more information about the overall reaction mechanism. The products distributions should detail whether or not the proposed isomerisation between *cis* and *trans* crotyl alcohol and 3-buten-ol is possible, and hence give stronger evidence for an overall reaction mechanism proposed later in this thesis, in Chapter 6.

The mono-substituted alkynes and alkene reactions in this section that employed the 1% Pd/C catalyst were Figures 5.8.1, 5.8.2, and 5.8.3, their reaction reagents were 2-butyne-1-ol, 3-butyne-1-ol, 3-buten-1-ol

respectively. A reaction profile for an experiment employing the 1% Pd/Al_2O_3 (nitrate precursor) catalyst with 2-butyne-1-ol is detailed in Figure 5.8.4.

Tables 5.8.1, 5.8.2, 5.8.3 detail a summary of the reaction data, and Figures 5.8.1, 5.8.2, 5.8.3 show reaction profiles for ambient pressure reactions employing the 1% Pd/C catalyst with 2-butyne-1-ol, 3-butyne-1-ol and 3-buten-1-ol respectively. Tables 5.8.4, details a summary of the reaction data, and Figures 5.8.4, shows the reaction profile for ambient pressure reaction employing the 1% Pd/Al_2O_3 (nitrate precursor) catalyst and 2-butyne-1-ol respectively.

Approximately 80mls of a 0.286M solution of 2-butyne-1-ol in propan-2-ol was used in Figures 5.8.1 and 5.8.4. Approximately 80mls of a 0.286M solution of 3-butyne-1-ol in propan-2-ol was used in Figure 5.8.2. Approximately 80mls of a 0.278M solution of 3-buten-1-ol in propan-2-ol was used in Figure 5.8.3. The rest of the experimental procedure for the reactions in this section was the same as that detailed in Section 3.5 for an ambient pressure reaction employing programmed reduction of the catalyst.

Figure 5.8.1 reached a conversion of 2-butyne-1-ol of 97.71% in 1320 minutes. A selectivity in the order of 40% towards the formation of *trans*-crotyl alcohol was maintained up to 97.51% conversion, with *trans*-crotyl alcohol being chosen to calculate the selectivity because it was the major product during the course of the reaction. Figure 5.8.2 reached a conversion of 3-butyne-1-ol of 89.23% in 320 minutes. A selectivity in the order of 95% towards the formation of 3-buten-1-ol was maintained up to 89.23% conversion. The change in position of the triple bond between 2-butyne-1-ol and 3-butyne-ol has significantly increased the rate of hydrogenation. Figure 5.8.3 reached a conversion of the 3-buten-1-ol of 59.57% in 1320 minutes. A selectivity in the order of 95% towards the formation of butanol was maintained up to 89.23% conversion. There is a selectivity in the order of 45% towards the formation of butanol initially, that is not maintained during the course of the reaction. The selectivity to butanol formation increases to around 70% at the end stages of the reaction. This increase is probably due to

the *cis* and *trans*-crotyl alcohol that has been formed during the course of the reaction being converted into butanol, and not enhanced selectivity to the formation of butanol from the 3-buten-1-ol.

Figure 5.8.4 reached a conversion of the 2-butyne-1-ol of 98.76% in 70 minutes. A selectivity in the order of 90% towards the formation of *trans*-crotyl alcohol was maintained up to 88.77% conversion. This compares favourably in terms of reaction rate and selectivity towards the formation *trans*-crotyl alcohol to Figure 5.8.1. The initial rate of hydrogenation for Figures 5.8.1, 5.8.2, 5.8.3 and 5.8.4 was $1.27x10^{-5}$, $5.32x10^{-5}$, $7.93x10^{-6}$ and $2.11x10^{-4}$ moles/l/s/g catalyst. The final mass balance for Figures 5.8.1, 5.8.2, 5.8.3 and 5.8.4 were 77.85, 80.87, 78.88 and 99.09% respectively. Figure 5.8.5 a), b), c) and d) are the mass-balance for Figures 5.8.1, 5.8.2, 5.8.3 and 5.8.4 respectively.

There was no formation of iso-propoxytetrahydrofuran observed during the course of any of the reactions detailed in this section as has been observed when using 2-butyne-1,4-diol in Section 5.2. There is however, (minor) formation of 1-(2-propanyloxy)-butan-1-ol that has been observed in the elevated pressure reactions that are detailed in Section 5.2 Figures 5.2.4, 5.2.5 and 5.2.6, but never up to this point in ambient pressure reactions. From the results in this section it is clear that a diol functionality present in the starting reagent is required to for the formation of iso-propoxytetrahydrofuran, without the diol functionality present in the starting reagent there can be no formation of iso-propoxytetrahydrofuran.

Table 5.8.1 Ambient pressure reaction employing the 1% Pd/C catalyst with 2-butyne-1-ol

Time (minutes)	2-butyne-1-ol (moles/l)	Butanol (moles/l)	*Cis*-crotyl alcohol (moles/l)	*T*-crotyl alcohol (moles/l)	3-butene-1-ol (moles/l)	1-(2-propanoxy) (moles/l)	Conversion (%)	Selectivity (%)
0	0.2838	0	0	0	0	0	0	0
30	0.2719	0.0005	0	0.0052	0	0	4.20	43.66
60	0.2579	0.0010	0	0.0083	0	0	9.12	31.91
90	0.2513	0.0017	0	0.0110	0	0	11.46	33.83
120	0.2451	0.0004	0	0.0139	0.0036	0	13.62	35.83
150	0.2366	0.0051	0.0025	0.0196	0.0037	0.0001	16.64	41.49
180	0.2303	0.0024	0.0027	0.0271	0.0037	0.0002	18.86	50.73
210	0.2251	0.0042	0.0035	0.0062	0.0039	0.0004	20.67	10.52
240	0.2204	0.0045	0.0039	0.0333	0.0040	0.0007	22.32	52.52
270	0.2140	0.0043	0.0040	0.0365	0.0041	0.0010	24.59	52.31
300	0.1986	0.0026	0.0041	0.0360	0.0042	0.0015	30.02	42.26
360	0.1929	0.0068	0.0042	0.0335	0.0046	0.0019	32.02	36.82
1260	0.0322	0.0525	0.0467	0.0783	0.0167	0.0051	88.64	31.12
1320	0.0071	0.0528	0.0477	0.0790	0.0171	0.0138	97.51	28.56
1440	0.0049	0.0535	0.0471	0.0847	0.0169	0.0138	98.28	30.37

Figure 5.8.1 Reaction profile for an ambient pressure reaction employing the 1% Pd/C catalyst with 2-butyne-1-ol

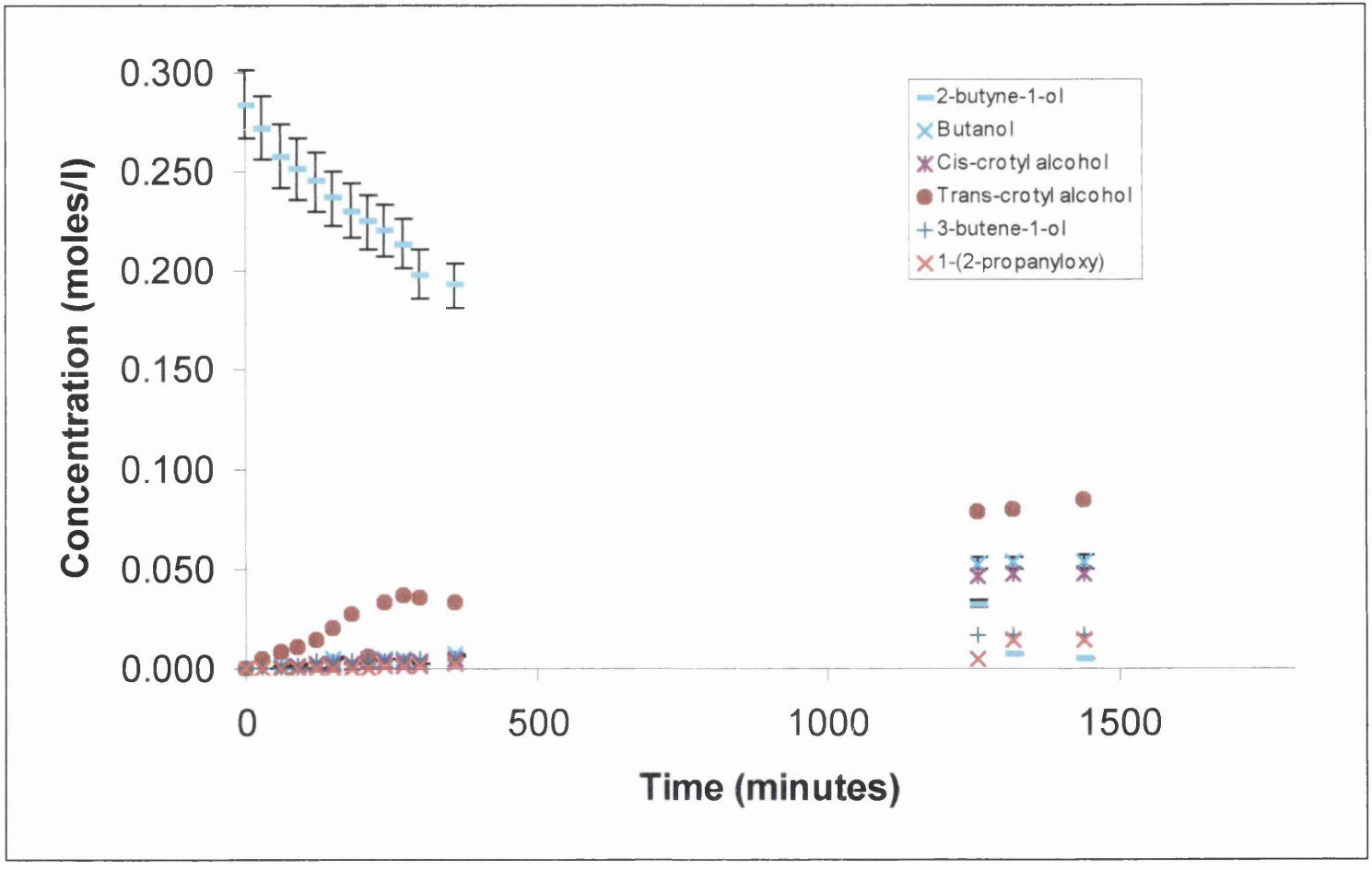


Table 5.8.2 Ambient pressure reaction employing the 1% Pd/C catalyst with 3-butyne-1-ol

Time (minutes)	3-Butyne-1-ol	Butanol (moles/l)	*Cis*-crotyl alcohol (moles/l)	*T*-crotyl alcohol (moles/l)	3-buten-1-ol (moles/l)	1-(2-propanoxy) (moles/l)	Conversion (%)	Selectivity (%)
0	0.2764	0	0	0	0	0	0	0
20	0.2670	0.0011	0	0	0.0084	0	3.40	89.29
40	0.2580	0.0011	0	0	0.0165	0	6.65	89.89
60	0.2477	0.0024	0	0	0.0260	0.0005	10.40	90.57
80	0.2363	0.0039	0	0	0.0365	0.0005	14.52	90.97
100	0.2216	0.0057	0.0038	0	0.0522	0.0006	19.83	95.21
120	0.2102	0.0070	0.0039	0	0.0627	0.0006	23.96	94.71
140	0.1963	0.0092	0.0040	0	0.0774	0.0006	28.97	96.65
160	0.1807	0.0116	0.0041	0	0.0918	0.0006	34.64	95.88
180	0.1571	0.0142	0.0042	0	0.1140	0.0006	43.16	95.53
200	0.1365	0.0165	0.0045	0.0039	0.1392	0.0006	50.61	99.492
300	0.0298	0.0192	0.0047	0.0129	0.2277	0.0007	89.23	92.33
1320	0.0045	0.2016	0.0050	0.0000	0.0047	0.0079	98.38	1.73
1380	0.0041	0.2028	0.0051	0.0000	0.0045	0.0079	98.50	1.64
1440	0.0043	0.2017	0.0051	0.0000	0.0046	0.0079	98.45	1.69

Figure 5.8.2 Reaction profile for an ambient pressure reaction employing the 1% Pd/C catalyst with 3-butyne-1-ol

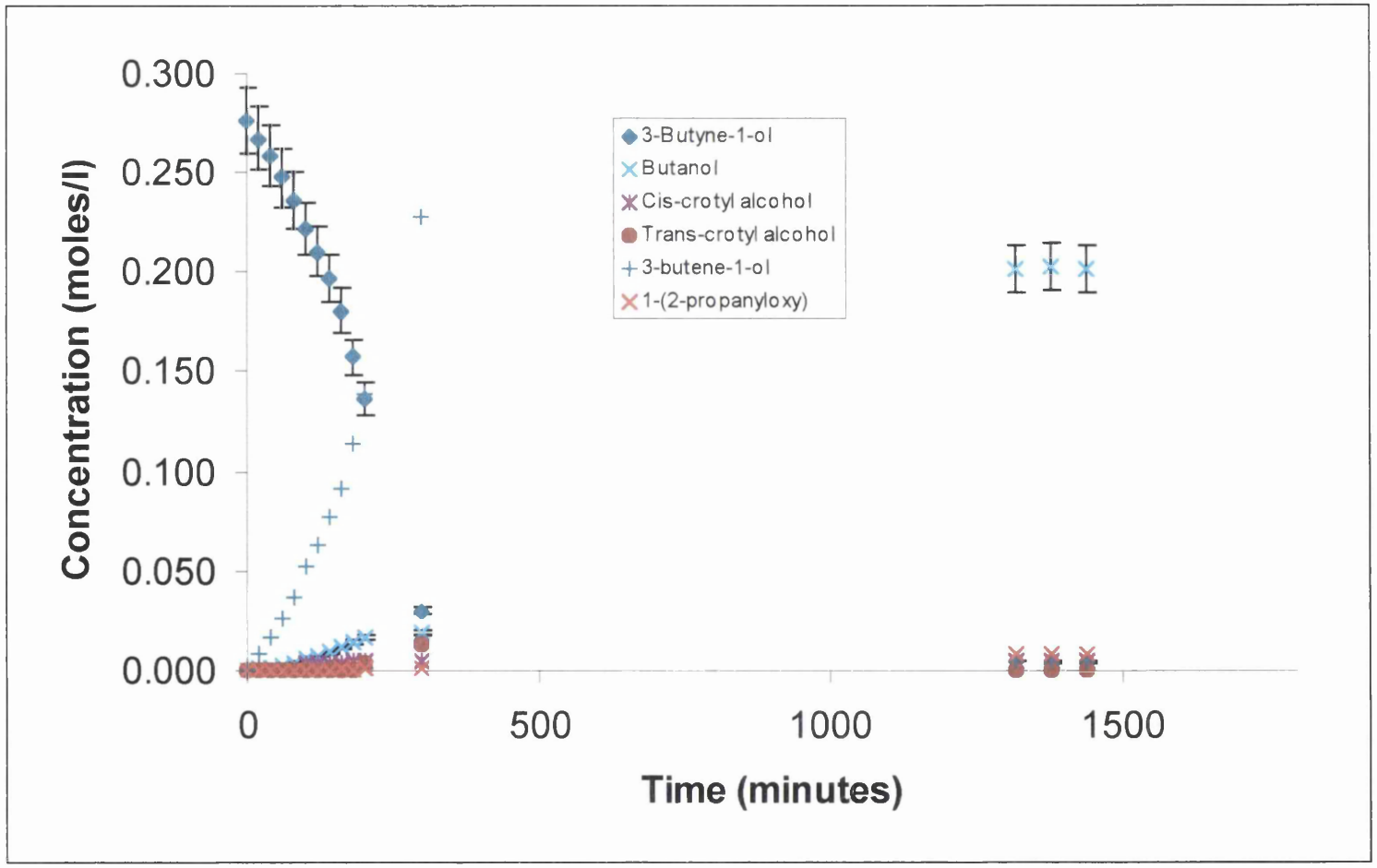


Table 5.8.3 Ambient pressure reaction employing the 1% Pd/C catalyst with 3-buten-1-ol

Time (minutes)	3-buten-1-ol (moles/l)	Butanol (moles/l)	*Cis*-crotyl alcohol (moles/l)	*T*-crotyl alcohol (moles/l)	1-(2-propanoxy) (moles/l)	Conversion (%)	Selectivity (%)
0	0.2682	0	0.0035	0.0035	0	0	0
20	0.2630	0.0010	0.0042	0.0039	0	1.91	18.58
40	0.2572	0.0045	0.0049	0.0048	0	4.10	41.20
60	0.2548	0.0057	0.0087	0.0058	0.0027	4.97	42.85
80	0.2510	0.0081	0.0094	0.0059	0.0019	6.40	47.02
100	0.2483	0.0092	0.0097	0.0065	0.0015	7.40	46.61
120	0.2455	0.0115	0.0111	0.0063	0.0013	8.46	50.61
140	0.2424	0.0118	0.0159	0.0097	0.0023	9.59	46.02
160	0.2396	0.0131	0.0227	0.0111	0.0030	10.66	45.90
180	0.2376	0.0240	0.0280	0.0145	0.0032	11.39	78.45
200	0.2307	0.0263	0.0274	0.0159	0.0034	13.98	70.20
300	0.2158	0.0285	0.0266	0.0130	0.0037	19.52	54.55
1320	0.1084	0.0761	0.0241	0.0156	0.0062	59.57	59.51
1380	0.0936	0.0801	0.0212	0.0156	0.0065	65.09	57.38
1440	0.0904	0.0836	0.0208	0.0157	0.0066	66.28	58.79

Figure 5.8.3 Reaction profile for an ambient pressure reaction employing the 1% Pd/C catalyst with 3-buten-1-ol

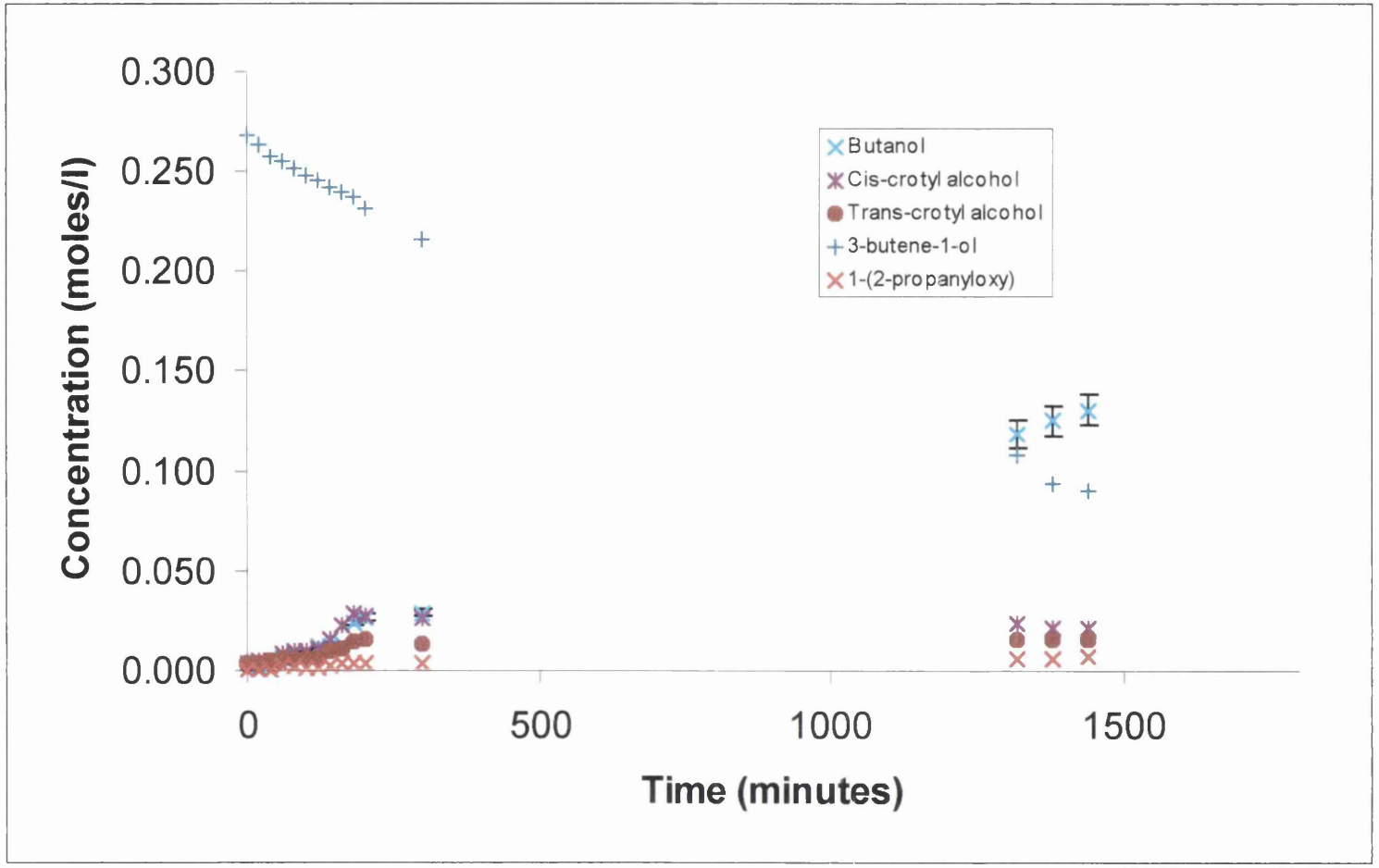


Table 5.8.4 Ambient pressure reaction employing the 1% Pd/Al_2O_3 (nitrate precursor) catalyst with 2-butyne-1-ol

Time (minutes)	2-butyne-1-ol (moles/l)	Butanol (moles/l)	*Cis*-crotyl alcohol (moles/l)	*T*-crotyl alcohol (moles/l)	3-butene-1-ol (moles/l)	1-(2-propanoxy) (moles/l)	Conversion (%)	Selectivity (%)
0	0.2278	0	0	0	0	0	0	0
10	0.1831	0.0005	0	0.0256	0	0	19.63	57.36
20	0.1516	0.0014	0	0.0686	0	0	33.47	89.92
30	0.1247	0.0030	0	0.0916	0	0	45.25	88.81
40	0.0918	0.0039	0	0.1213	0.0036	0	59.76	89.12
50	0.0657	0.0049	0.0046	0.1512	0.0038	0.0002	71.18	93.27
60	0.0256	0.0070	0.0089	0.1770	0.0041	0.0002	88.77	87.50
70	0.0028	0.0661	0.0197	0.0462	0.0119	0.0124	98.76	20.54
90	0.0011	0.1424	0.0597	0.0149	0.0083	0.0027	99.54	6.59
100	0.0009	0.1871	0.0198	0.0130	0.0051	0.0048	99.59	5.72
120	0.0007	0.1884	0.0168	0.0098	0.0057	0.0073	99.70	4.30
140	0.0006	0.1883	0.0131	0.0081	0.0054	0.0093	99.72	3.55
160	0.0006	0.1895	0.0122	0.0077	0.0057	0.0115	99.73	3.38
180	0.0005	0.1829	0.0110	0.0071	0.0039	0.0140	99.79	3.12
195	0.0005	0.1869	0.0106	0.0060	0.0055	0.0163	99.78	2.64

Figure 5.8.4 Reaction profile for an ambient pressure reaction employing the 1% Pd/Al_2O_3 (nitrate precursor) catalyst with 2-butyne-1-ol

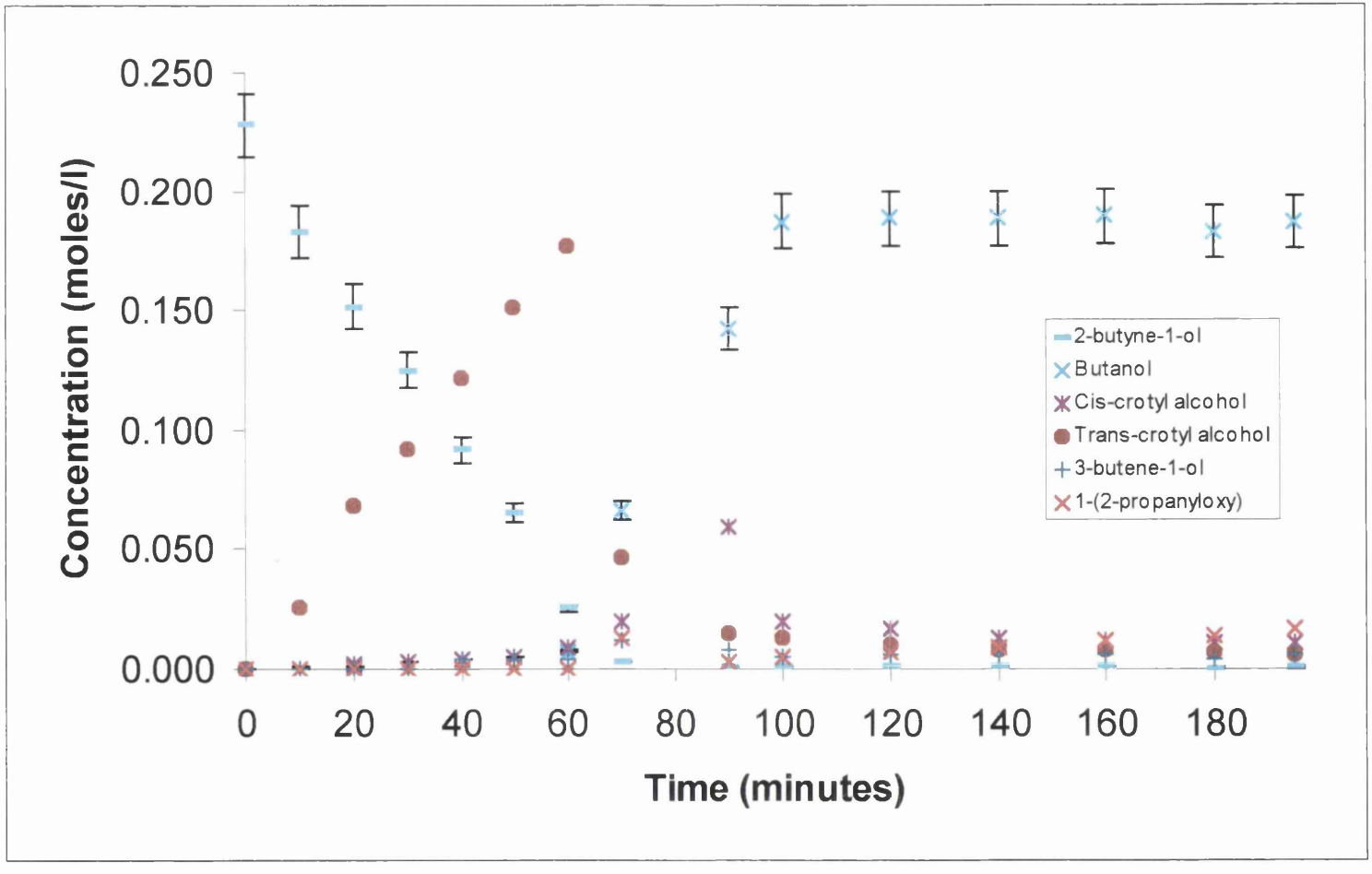
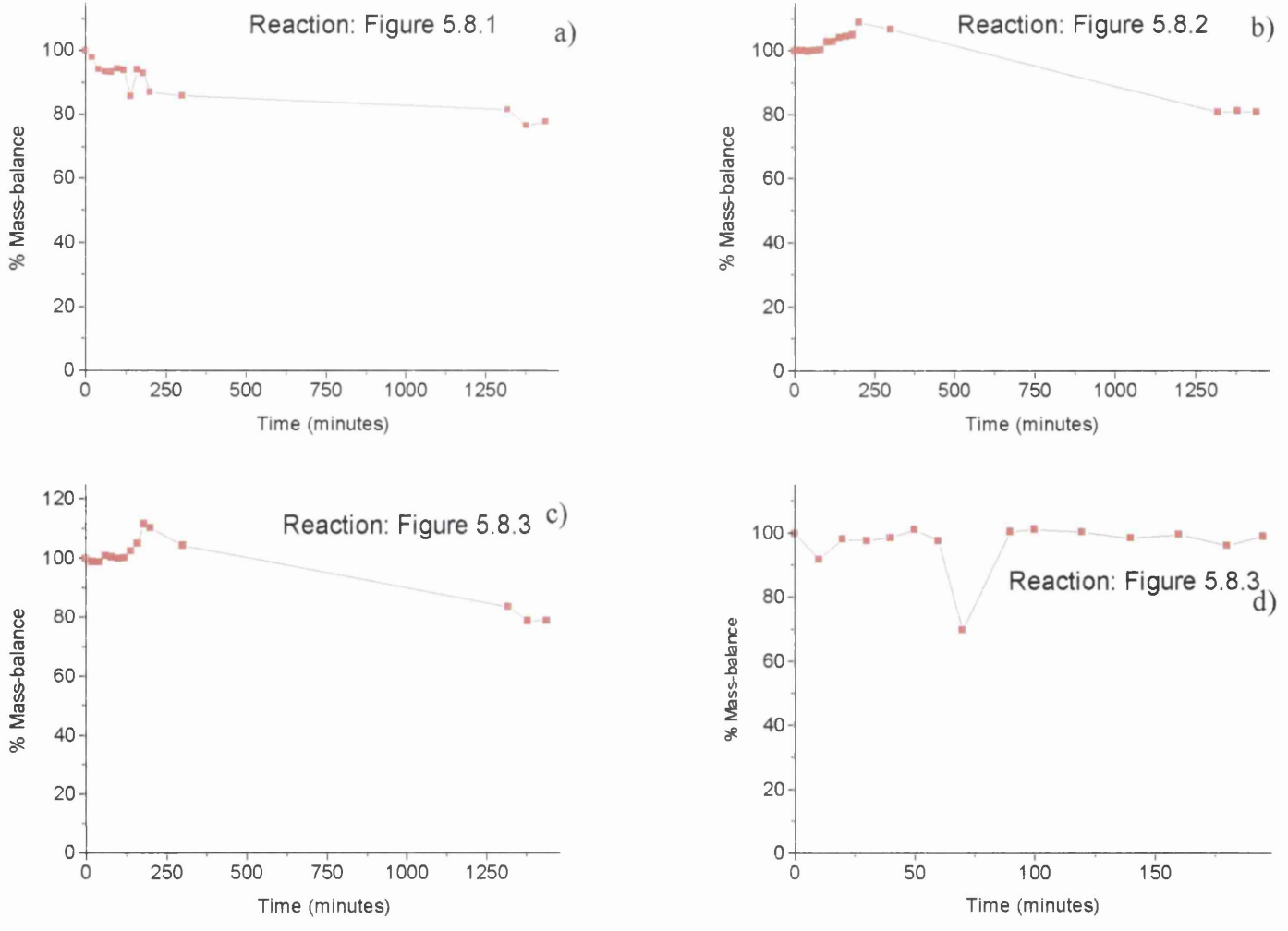


Table 5.8.5 Summary for Section 5.8

Reaction	Reagent	Rate of reaction (moles/l/s/g catalyst)	T.O.F (moles/l/s/ Pd surface)	Final product order	Final % mass-balance	% Conversion at t=100 minutes
Figure 5.8.1 (1% Pd/C)	2-butyne-1-ol	1.27×10^{-5}	2.35×10^{-24}	*Trans*-crotyl, butanol, *cis*-crotyl and 3-buten-1-ol	77.85	12.18
Figure 5.8.2 (1% Pd/C)	3-butyne-1-ol	5.32×10^{-5}	9.83×10^{-24}	Butanol, 1-(2-propanyloxy)-butan-1-ol, *cis*-crotyl alcohol and 3-buten-1-ol	80.87	19.83
Figure 5.8.3 (1% Pd/C)	3-buten-1-ol	7.93×10^{-6}	1.47×10^{-24}	Butanol, *cis*-crotyl, *trans*-crotyl alcohol and 1-(2-propanyloxy)-butan-1-ol	78.88	7.40
Figure 5.8.4 (1% Pd/Al_2O_3 (nitrate precursor))	2-butyne-1-ol	2.11×10^{-4}	3.90×10^{-24}	Butanol, 1-(2-propanyloxy)-butan-1-ol, *cis*-crotyl and *trans*-crotyl alcohol	99.09	99.59 (98.76% by 70 minutes)

Figure 5.8.5 Mass-balances for reactions from Section 5.8



5.8.1 Discussion for mono-substituted alkynes and 3-buten-1-ol

All the mono-substituted alkynes and alkene experiments detailed in this section underline the fact that a diol species is required at the start of the reaction in order to produce iso-propoxytetrahydrofuran. The product that is produced in the place of iso-propoxytetrahydrofuran is 1-(2-propanyloxy)-butan-1-ol in the reactions in this Section. If we consider the elevated pressure reactions in Section 5.2 (Figures 5.2.4, 5.2.5 and 5.2.6) in concert with the reactions in this Section, the production of 1-(2-propanyloxy)-butan-1-ol seems likely to occur by the same (or similar) mechanism in the reactions in both Sections. In the elevated pressure reactions in Section 5.2, the elevated pressure leads to the formation of 1-(2-propanyloxy)-butan-1-ol, in the reactions in this section it is due to the reaction reagent not having a diol functionality.

The formation of iso-propoxytetrahydrofuran must occur through a solvent interaction with an adsorbed species on the catalyst active sites (Figures 5.2.7, 5.2.8, 5.2.9 and 5.2.10 show that there is no reaction when there is no catalyst present). The only source of the iso-propoxy group is the reaction solvent, there is no evidence of any C-3 alcohols other than propan-2-ol during the course of the reaction. This means that a C-4 species adsorbed on the catalyst active sites must undergo a reaction with the adsorbed iso-propoxy group derived from the reaction solvent. A similar process of solvent interaction with adsorbed reaction intermediate is likely to be responsible for the formation of 1-(2-propanyloxy)-butan-1-ol.

If all the reactions detailed in this section are allowed to continue until there is no further reaction then butanol will be the major product at 200% conversion, (only Figures 5.8.2 and 5.8.4 were continued until no further reaction occurred). When the reaction reagent was 2-butyne-1-ol as in Figures 5.8.1 and 5.8.4 the major product produced up to 100% conversion of 2-butyne-1-ol was *trans*-crotyl alcohol. In Figure 5.8.2 when 3-butyne-1-ol was employed as the reaction solvent the main product up to 100% conversion was 3-buten-1-

ol. In Figure 5.8.3 when 3-buten-1-ol was employed as the reaction solvent the main product up to 66.28% conversion was butanol.

In all the reactions in this section there was *cis* and *trans*–crotyl alcohol and 3-buten-1-ol produced during the reaction profile. This shows that there is isomerisation and double bond shifts on the catalyst surface during the course of the reaction. Figure 5.8.3 best illustrates this point. Without a double bond and isomerisation (bond rotation) there could be no formation of *cis* and *trans*-crotyl alcohol. If there is isomerisation between *cis* and *trans*-crotyl alcohol and 3-buten-ol, then this is very likely to occur through a common intermediate or intermediates. When *cis* or *trans*-crotyl alcohol and 3-buten-ol are produced in the reaction they can desorb form the catalyst surface, they are also able to re-adsorb to isomerise and/or go onto form butanol. This is consistent with the experimental observations made in Section 5.2, 5.3 and 5.6 where we see varying concentrations of *cis* or *trans*-crotyl alcohol and 3-buten-ol throughout the reaction profiles (Chapter 6 has a more detailed discussion about the isomerisation involved in the reaction mechanism).

If we look at Table 5.8.5 we can see a distinct difference in the reaction rates for Figure 5.8.1 and 5.8.2, 1.27×10^{-5} and 5.32×10^{-5} moles/l/s/g catalyst respectively. Figures 5.8.1 and 5.8.2 used the same reaction protocol. The change in the position of the triple bond to the "3" position instead of the "2" position in the backbone of the starting reagent has led to the hydrogenation rate being approximately 4 times quicker (this is also reflected by the difference in the T.O.Fs). The rate of hydrogenation of 3-buten-1-ol in Figure 5.8.3 is 7.93×10^{-6} moles/l/s/g catalyst this rate is approximately 7 times slower than that in Figure 5.8.2 when 3-butyne-1-ol was employed.

The rate of hydrogenation when the 1% Pd/Al_2O_3 (nitrate precursor) catalyst (Figure 5.8.4) was employed to hydrogenate 2-butyne-1-ol increased in comparison to Figure 5.8.1 when the 1% Pd/C catalyst was employed. This rate increase from 1.27×10^{-5} in Figure 5.8.1 to 2.11×10^{-4} moles/l/s/g catalyst in Figure 5.8.4 can be mostly attributed to the increase in dispersion, and hence an increased number of active sites on the catalyst surface. Comparing the

T.O.F. values for Figures 5.8.1 and 5.8.4 we can see that it may also have something to do with the average metal particle size of the palladium on the 1% Pd/Al_2O_3 (nitrate precursor) catalyst, with the smaller palladium particles being partially responsible for an increased hydrogenation rate in Figure 5.8.4. The average metal particle size for the 1% Pd/C catalyst is 11.41nm, for the 1% Pd/Al_2O_3 catalyst the average metal particle size is 1.15nm.

Another way to illustrate the differences in the rate of reaction is to compare the % conversion at 100 minutes in the reaction for the four reactions in this section on Table 5.8.5. Figure 5.8.1, 5.8.2 and 5.8.3 have 12.18, 19.83 and 7.40% conversion of the starting reagent at 100 minutes. Figure 5.8.4 has 99.59% conversion at 100 minutes into the reaction, full conversion of 2-butyne-1-ol was effectively reached in closer to 70 minutes.

Figure 5.8.5 a), b), c) and d) detail the mass-balance profiles for Figures 5.8.1, 5.8.2, 5.8.3 and 5.8.4 respectively. The final mass-balances for Figures 5.8.1, 5.8.2, 5.8.3 and 5.8.4 were 77.85, 80.87, 78.88 and 99.09% respectively. Figure 5.8.5 a), b), c) and d) are the mass-balances for Figures 5.8.1, 5.8.2, 5.8.3 and 5.8.4 respectively. If we compare the mass balance for Figures 5.8.1, 5.8.2 and 5.8.3 with that of Figure 5.2.1 from Section 5.2 (70.61%), we can see that the mass-balance for reactions in this section that employed the 1% Pd/C catalyst are more complete. Having the starting reagent as a mono-substituted alkyne or alkene seems to slightly impair the ability of the surface bound reaction intermediates to form butane and butene when the 1% Pd/C catalyst is employed. The mass-balance for Figure 5.8.4 is effectively complete at 99.09%, this is in agreement with the mass-balance in Figure 5.7.2. Having a smaller average size of metal particles seems to inhibit the formation of butane and butene.

5.8.2 SUMMARY FOR SECTION 5.8

- None of the experiments in this section produced any iso-propoxytetrahydrofuran. The diol functionality in the reaction reagent is required to produce iso-propoxytetrahydrofuran.

- 1-(2-propanyloxy)-butan-1-ol was produced instead of iso-propoxytetrahydrofuran but in relatively small quantities.

- The position of the triple bond in the reaction reagent can have a pronounced effect on the rate of hydrogenation and T.O.F.

- All the experiments in this section had cis and trans-crotyl alcohol and 3-buten-1-ol in their reaction profiles, this was due to isomerisation of adsorbed species on the catalyst surface.

- The mass-balances for all the reactions in this section that employed the 1% Pd/C catalyst were more complete than the mass-balances in Section 5.2. This suggests that the formation of butane and butene is less favourable when a mono-substituted alkyne or alkene is employed as the reaction reagent.

- As in Section 5.7, when the 1% Pd/Al_2O_3 (nitrate precursor) catalyst was employed for hydrogenation, it had an effectively complete mass-balance.

5.9 HYDROGENATION OF 2-BUTYNE-1,4-DIOL EMPLOYING THE 9.1% Cu/SiO_2 CATALYST

A wide variety of high added value and low volume processes, as well as large scale processes such as the water gas shift reaction and methanol synthesis employ copper-based catalysts [32, 33, 34]. In situations where high selectivities are of primary importance, copper catalysts have become the catalyst of choice for certain hydrogenation reactions, such as the hydrogenation of unsaturated carbonyl compounds [35, 36]. One of the disadvantages with copper catalysts is the tendency of metal particles to agglomerate, this can result in a decrease in the catalytic activity due to a decrease in the available metal surface area. At approximately one third of copper's melting point (179^0C) in Kelvin, the Hüttig temperature denotes the start on significant surface mobility [1].

Recent work in our laboratories has concentrated on nitrobenzene hydrogenation to aniline using supported copper catalysts [1]. That work used a series of silica supported copper catalysts and showed that while the rate of reaction was modest by comparison to other metal catalysts, the selectivity was superior. A major milestone in that work was the development of a protocol to activate catalysts so that they could successfully operated in liquid phase hydrogenations. It was decided to evaluate one of these Cu/SiO_2 catalysts for the selective hydrogenation of 2-butyne-1,4-diol.

It is hoped that using a supported copper catalyst will enable the hydrogenation of 2-butyne-1,4-diol to be carried out more selectively to 2-butene-1,4-diol during the first stage of the reaction, with fewer "side products" observed in the final product distributions. The reaction rate for the reactions in this section are expected to be slower than those in reactions that employ one of the supported palladium catalysts, but with the possibility of fewer "side products". There is also the distinct possibility that iso-propoxytetrahydrofuran will not be produced during the course of the reaction. A different solvent interaction with an adsorbed species on the

catalyst surface might occur and may produce a different reaction product from any that have been observed up to this point, in any of the reactions that employed the supported palladium catalysts. The reactions detailed in this were conducted in both the i) ambient and ii) elevated pressure reaction vessels.

Tables 5.9.1 and 5.9.2 detail a summary of the reaction data, and Figures 5.9.1 and 5.9.2 shows a reaction profiles for ambient pressure reactions employing the 9.1% Cu/SiO_2 catalyst with 2-butyne-1,4-diol, and *cis*-2-butene-1,4-diol respectively. The catalyst was activated following the procedure developed by D.S. Anderson [1].

i) Ambient Pressure Reactions

For both of the ambient pressure detailed experiments in this section the experimental procedure was the same as that detailed in Section 3.5 for an ambient pressure reaction that employs a copper catalyst. These experiments only reached a conversion of 2-butyne-1,4-diol of 11.77% (Figure 5.9.1) and a conversion of *cis*-2-butene-1,4-diol of 10.61% (Figure 5.9.2) in 28 hours respectively. This was considerably lower than the amount of conversion that would be seen in an ambient pressure reaction employing the 1% Pd/C catalyst over a shorter period of time. Indeed it only takes approximately 720 minutes to hydrogenate all the 2-butyne-1,4-diol when the 1% Pd/C catalyst is employed. The rate of hydrogenation for Figures 5.9.1 and 5.9.2 was $3.13x10^{-7}$ and $3.09x10^{-7}$ moles/l/s/g catalyst, this is far slower than the rate that was observed when the 1% Pd/C catalyst was employed (Figure 5.2.1), its rate was $1.96x10^{-5}$ moles/l/s/g catalyst for 2-butyne-1,4-diol hydrogenation. There was a high selectivity in the order of 98% towards the formation of *cis*-2-butene-1,4-diol (Figure 5.9.1), and 98% towards the formation of butane-1,4-diol (Figure 5.9.2) that was maintained during the course of the reaction. This was superior to the selectivity that has previously been observed when employing the 1% Pd/C catalyst in the ambient reaction vessel which was normally around 95% (Figure 5.2.1). The selectivity to formation of butane-

1,4-diol form *cis*-2-butene1-,4-diol for Figure 5.9.2 was far higher than a corresponding reaction (Figure 5.2.2) that employed the 1% Pd/C catalyst to hydrogenate *cis*-2-butene-1,4-diol. There was no formation of butane-1,4-diol for Figure 5.9.1. Butanol, *cis* or *trans* crotyl alcohol, 3-buten-1-ol or iso-propoxytetrahydrofuran were not observed during the course of the reaction for Figures 5.9.1 and 5.9.2, these products usually being observed when using 2-butyne-1,4-diol and the 1% Pd/C catalyst in previous experiments.

The mass balance for the ambient pressure reactions in this section were effectively complete. For Figure 5.9.1 the final mass balance was 99.88% (Figure 5.9.3 a), and for Figure 5.9.2 the final mass balance was 99.99% (5.9.3 b). These final mass balances compare favourably with the final mass balance for Figure 5.2.1 was 70.61% (Figure 5.9.3 c).

ii) Elevated Pressure Reactions

The previous two reactions detailed in Figures 5.9.1 and 5.9.2 show ambient pressure reactions that were conducted with the 9.1% Cu/SiO_2 catalyst. The ambient pressure reactions that utilised the 9.1% Cu/SiO_2 catalyst showed that supported copper catalysts could possibly, with further optimisation provide a successful replacement to the 1% Pd/C catalyst used for the bulk of the investigations detailed here, with improved selectivity. When the 1% Pd/C catalyst was first employed in the elevated pressure reaction vessel for the selective hydrogenation of 2-butyne-1,4-diol to *cis*-2-butene-1,4-diol, an enhanced reaction rate was observed (as outlined in Section 5.2). The main divergence from the selectivity and product distributions that were observed at elevated pressure was the formation of 1-(2-propanyloxy)-butan-1-ol.

For the elevated pressure reactions that employed the 9.1% Cu/SiO_2 catalyst, the experimental procedure was the same as that detailed in Section 3.6 for an *ex*-situ reduction of catalyst. The experiments showed no conversion of the 2-butyne-1,4-diol over 28 hours. No reaction was detected in the elevated pressure reaction vessel, with no material detected in the reaction samples

other than the reaction solvent (propan-2-ol) and the reaction reagent 2-butyne-1,4-diol. The catalyst was completely inactive over the 28 hour period the reaction was allowed to run. The experiments were probably unsuccessful due to problems with the catalyst activation. Several different weights of catalyst were tried, ranging from 4g down to 0.5g. Different flows of reduction gas were also tried, form 300ml/minute down to 30ml/minute. Changing the flow of the reducing gas also had no impact on the catalyst activity, *i.e.* no activity observed in transferring to an elevated pressure regime.

Table 5.9.1 Ambient pressure reaction employing the 9.1% Cu/SiO_2 catalyst

Time (hours)	Butyne-1,4-diol (moles/l)	Butene-1,4-diol (moles/l)	Butane-1,4-diol (moles/l)	Butanol (moles/l)	*Cis*-crotyl alcohol (moles/l)	*T*-crotyl alcohol (moles/l)	3-butene-1-ol (moles/l)	Iso-propoxythf (moles/l)	Conversion (%)	Selectivity (%)
0	0.2178	0	0	0	0	0	0	0	0	0
1	0.2168	0.0010	0	0	0	0	0	0	0.46	96.08
2	0.2160	0.0018	0	0	0	0	0	0	0.86	98.24
3	0.2150	0.0028	0	0	0	0	0	0	1.31	98.94
4	0.2139	0.0038	0	0	0	0	0	0	1.78	97.39
5	0.2131	0.0047	0	0	0	0	0	0	2.17	99.55
6	0.2120	0.0056	0	0	0	0	0	0	2.65	97.13
7	0.2110	0.0065	0	0	0	0	0	0	3.11	95.74
8	0.2101	0.0074	0	0	0	0	0	0	3.52	96.99
23	0.1971	0.0200	0	0	0	0	0	0	9.50	96.72
24	0.1960	0.0214	0	0	0	0	0	0	9.99	98.18
25	0.1951	0.0223	0	0	0	0	0	0	10.42	98.36
26	0.1942	0.0232	0	0	0	0	0	0	10.85	98.36
27	0.1932	0.0242	0	0	0	0	0	0	11.29	98.56
28	0.1922	0.0254	0	0	0	0	0	0	11.77	98.99

Figure 5.9.1 Reaction profile for an ambient pressure reaction employing the 9.1% Cu/SiO_2 catalyst

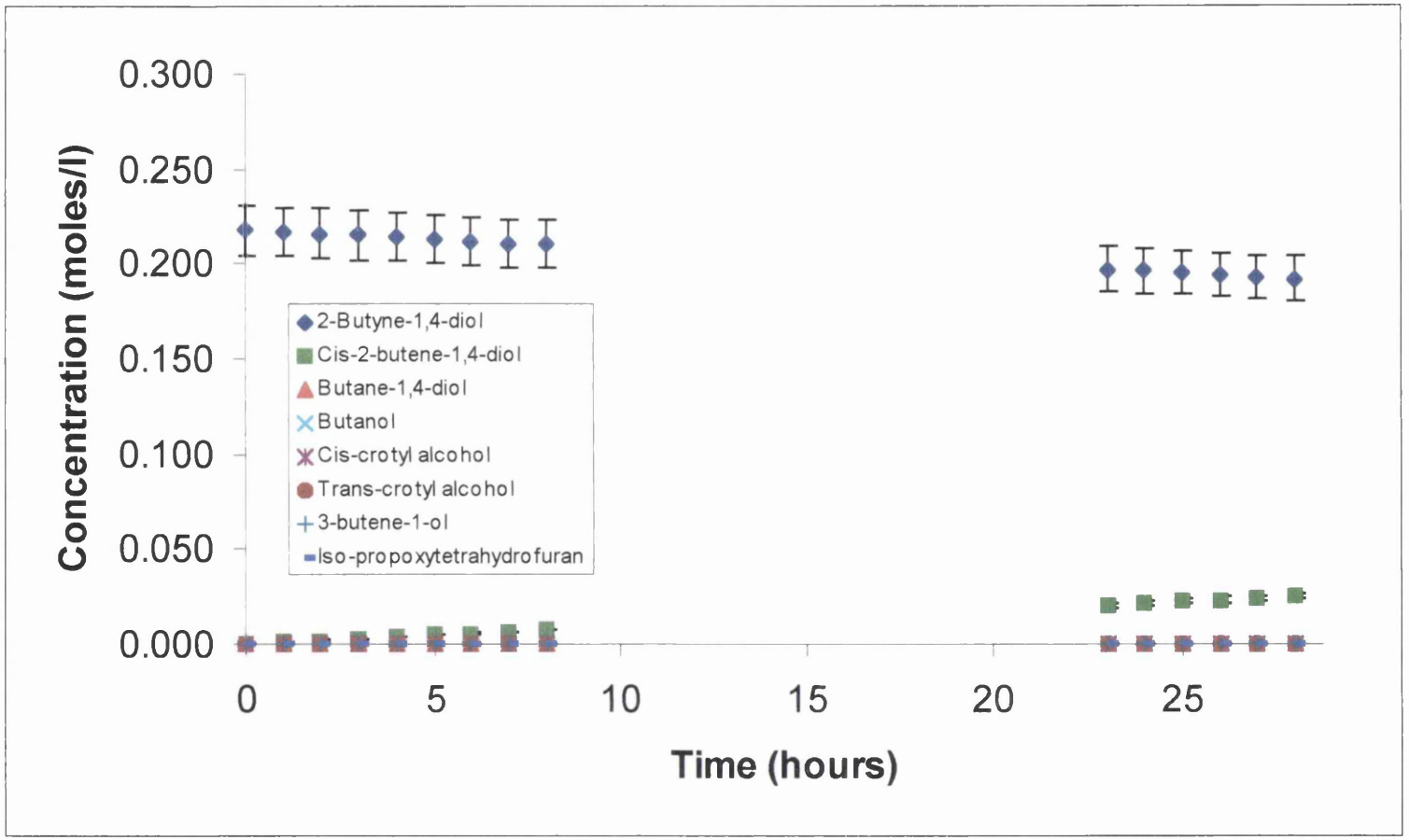


Table 5.9.2 Ambient pressure reaction employing the 9.1% Cu/SiO_2 catalyst and *cis*-2-butene-1,4-diol

Time (hours)	Butene-1,4-diol (moles/l)	Butane-1,4-diol (moles/l)	Butanol (moles/l)	*Cis*-crotyl alcohol (moles/l)	*T*-crotyl alcohol (moles/l)	3-butene-1-ol (moles/l)	Iso-propoxythf (moles/l)	Conversion (%)	Selectivity (%)
0	0.2274	0	0	0	0	0	0	0	0
1	0.2271	0.0003	0	0	0	0	0	0.13	95.15
2	0.2262	0.0012	0	0	0	0	0	0.56	95.46
3	0.2250	0.0024	0	0	0	0	0	1.08	98.06
4	0.2242	0.0032	0	0	0	0	0	1.40	99.62
5	0.2231	0.0043	0	0	0	0	0	1.90	99.49
6	0.2227	0.0047	0	0	0	0	0	2.06	99.57
7	0.2218	0.0053	0	0	0	0	0	2.45	95.82
8	0.2212	0.0061	0	0	0	0	0	2.72	99.54
23	0.2076	0.0193	0	0	0	0	0	8.70	97.69
24	0.2063	0.0207	0	0	0	0	0	9.27	97.99
25	0.2051	0.0216	0	0	0	0	0	9.81	96.72
26	0.2048	0.0225	0	0	0	0	0	9.95	99.28
27	0.2036	0.0234	0	0	0	0	0	10.47	98.41
28	0.2033	0.0241	0	0	0	0	0	10.61	99.91

Figure 5.9.2 Reaction profile for an ambient pressure reaction employing the 9.1% Cu/SiO_2 catalyst and *cis*-2-butene-1,4-diol

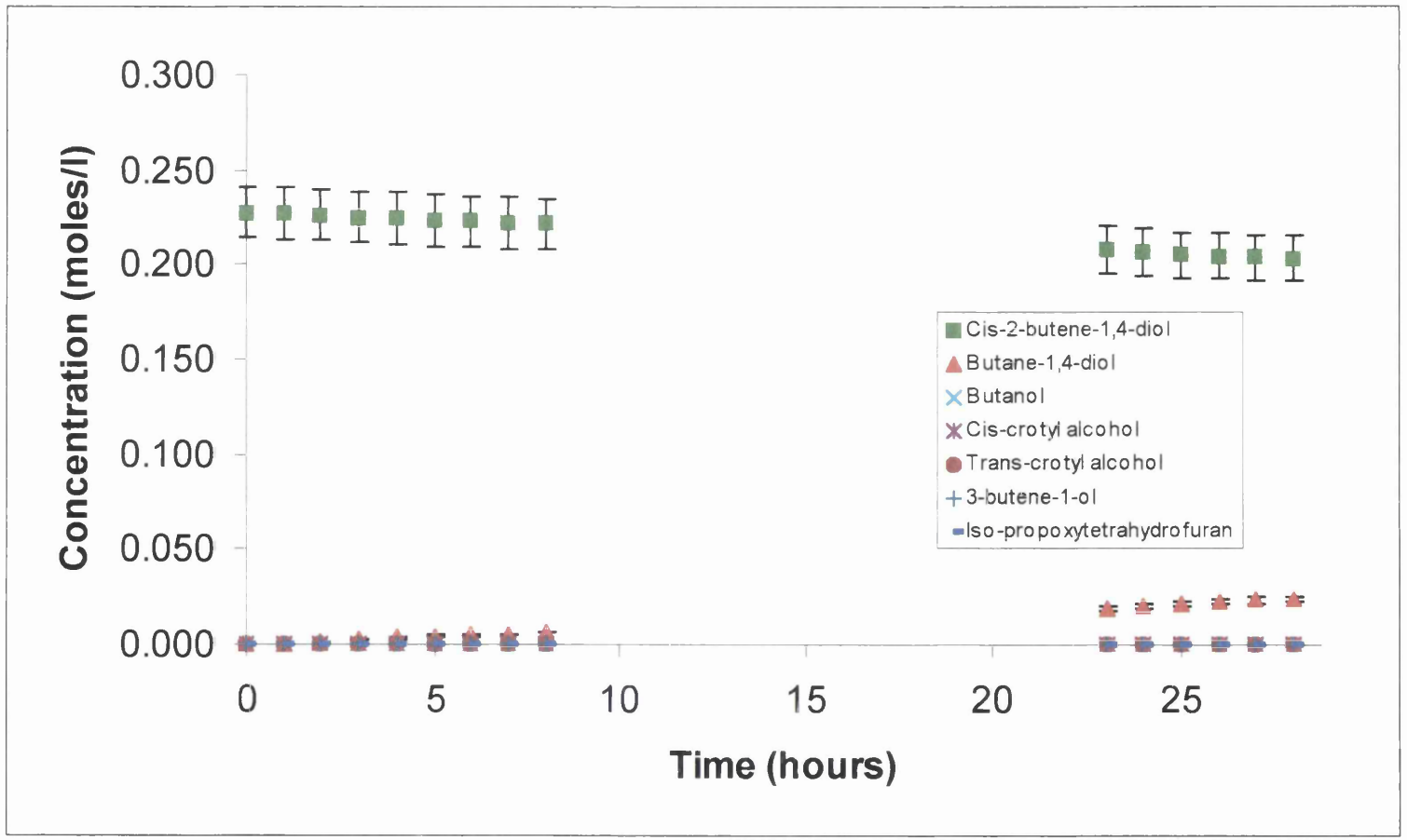
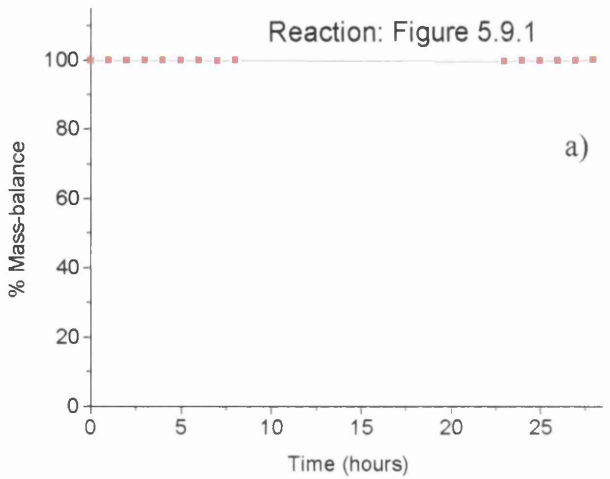
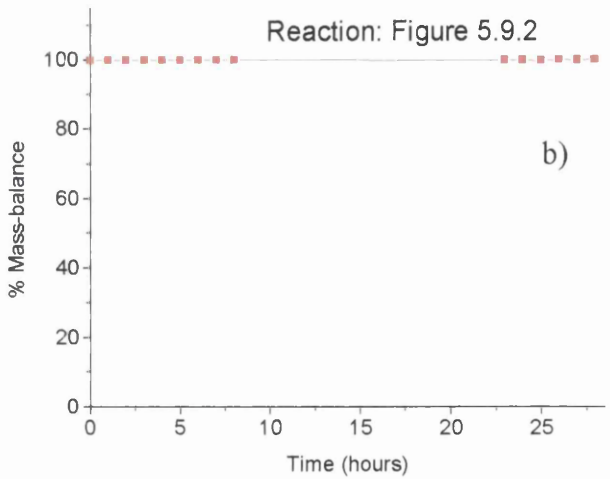


Figure 5.9.3 Mass-balances for reactions from Section 5.9 and Figure 5.2.1 form Section 5.2





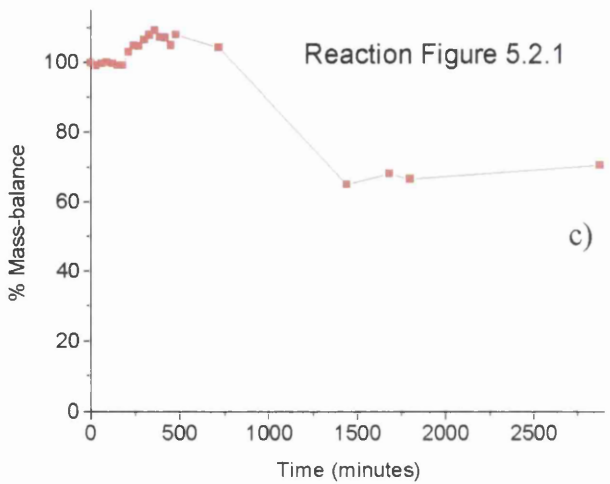
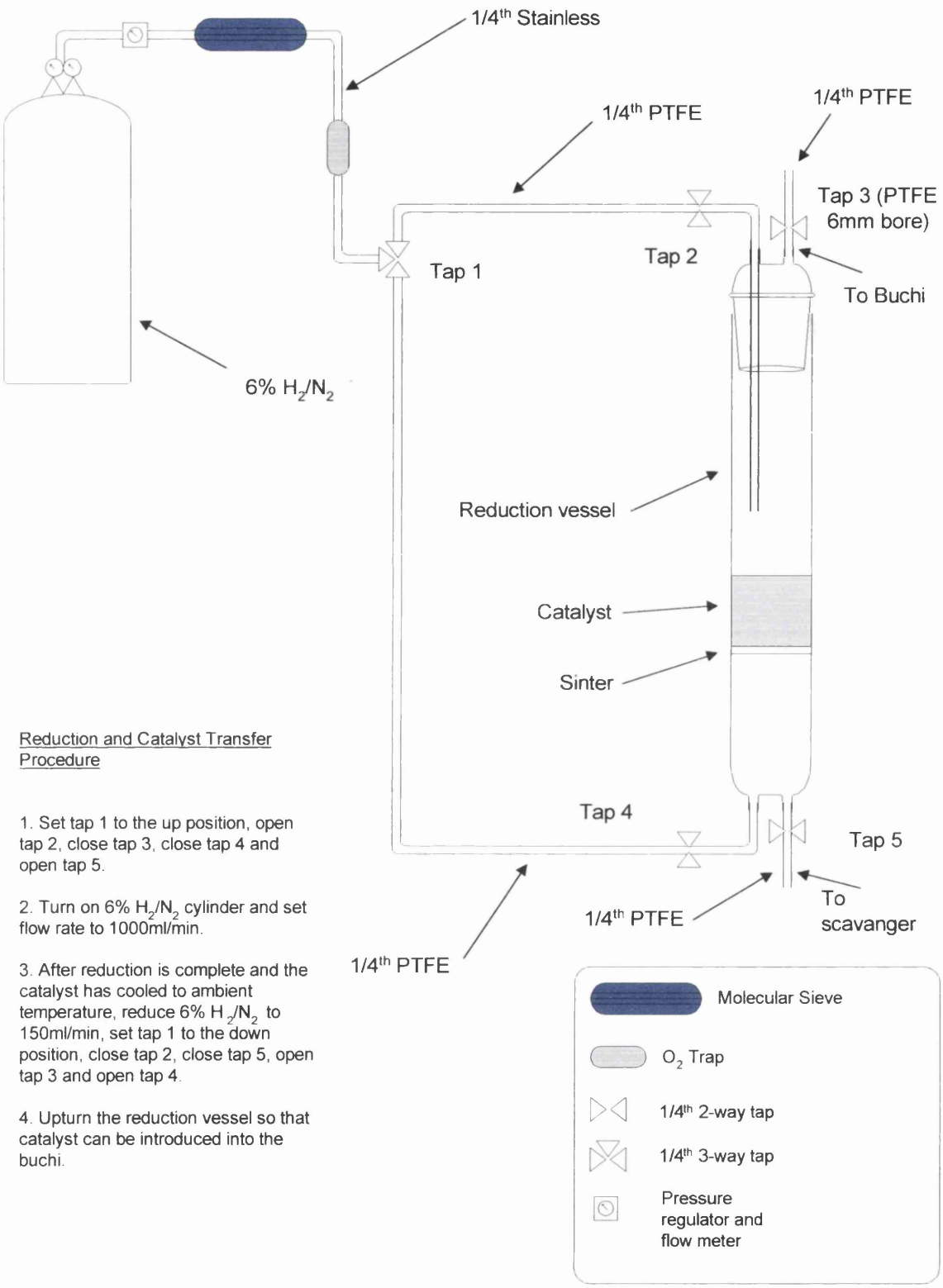


Figure 5.9.4 *Ex-situ* reduction apparatus for copper catalysts employing the elevated pressure reaction vessel



Reduction and Catalyst Transfer Procedure

1. Set tap 1 to the up position, open tap 2, close tap 3, close tap 4 and open tap 5.

2. Turn on 6% H_2/N_2 cylinder and set flow rate to 1000ml/min.

3. After reduction is complete and the catalyst has cooled to ambient temperature, reduce 6% H_2/N_2 to 150ml/min, set tap 1 to the down position, close tap 2, close tap 5, open tap 3 and open tap 4.

4. Upturn the reduction vessel so that catalyst can be introduced into the buchi.

5.9.1 Discussion for the hydrogenation of 2-butyne-1,4-diol employing the 9.1% Cu/SiO_2 catalyst

The supported copper catalyst was investigated to try to and maximise the selectivity to *cis*-2-butene-1,4-diol throughout the reaction. It was hoped that 9.1% Cu/SiO_2 catalyst would produce less unwanted "side products" (with higher selectivity to *cis*-2-butene-1,4-diol formation) such as n-butanol, *cis* and *trans* crotyl alcohol, 3-buten-1-ol, iso-propoxytetrahydrofuran.

In the ambient pressure reactor, using 1.0000g of the 9.1% Cu/SiO_2 catalyst, a 11.77% conversion of 2-butyne-1,4-diol was achieved in 28 hours (Figure 5.9.1), when *cis*-2-butene-1,4-diol was employed as the reaction reagent, a 10.61% conversion was achieved in 28 hours. Using 0.2500g of 1% Pd/C catalyst, 100% conversion of 2-butyne-1,4-diol is obtained in 12 hours. In light of the slow rate of hydrogenation in the ambient pressure reactor using the 9.1% Cu/SiO_2 catalyst, a series of experiments using the elevated pressure reactor were conducted. The elevated pressure reactor had previously been used to speed up the hydrogenation of 2-butyne-1,4-diol with the 1% Pd/C catalyst, the hydrogenation of 2-butyne-1,4-diol being approximately 6 times faster in the elevated pressure reactor. In this section with the 9.1% Cu/SiO_2 catalyst, no reaction was observed with any of the experiments attempted with the elevated pressure reactor. The mass balances for the reactions in this section are also more complete than for the reactions in Section 5.2 (*e.g.* Figure 5.2.1).

The studies with the copper catalyst highlight differences in the different reactors, and the differences in the catalysts. The ambient pressure reactor enables the catalyst to be readily reduced in the gas phase. The elevated pressure in the elevated pressure reactor should have produced greater activity, but activation of copper catalysts at high temperatures (> 200°C) is difficult. The relatively low Hüttig temperature (179°C) of copper can lead to significant surface mobility, *i.e.* increased possibility of agglomeration of surface copper.

The *ex-situ* reduction vessel (Figure 3.6.1) was not suitable for the complete reduction of the 9.1% Cu/SiO_2 catalyst. The 9.1% Cu/SiO_2 catalyst has a relatively low density, this lead to it taking up too much space in the *ex-situ* reduction vessel, so there was a problem of the catalyst sitting in the transfer tubing between the reduction vessel and the elevated pressure reactor during the reduction. The flow of 6% H_2/N_2 gas that was used drove the catalyst off the sinter and into the tubing, this led to poor reduction of the supported copper catalyst. In the transfer of the catalyst from the *ex-situ* reduction vessel to the elevated pressure reactor, it is quite likely that the existing *ex-situ* methodology is not suitable for supported copper catalysts.

Conversely, the *ex-situ* reduction of a 1% palladium catalysts is relatively easy when compared to the *ex-situ* reduction of the 9.1% Cu/SiO_2 catalyst. The reduction of the 1% palladium catalysts was possible in the reaction solvent at room temperature. Even if the 1% Pd/C catalyst was exposed to air, it will be re-reduced by hydrogen in the elevated pressure reactor. The ambient pressure reaction vessel is ideal for the reduction of the 9.11% Cu/SiO_2 catalyst as previous study here at Glasgow has shown [1]. The ability to reduce the catalyst within the reaction vessel when it is sitting on the sinter (Figure 3.5.2), enables the catalyst to be kept under of constant stream of gas, thus preventing oxidisation of the catalyst before the reagent solution is introduced. With the benefit of the constant gas flow in mind, a new *ex-situ* reduction vessel was designed for the reduction of supported copper catalysts for use with the elevated pressure reaction vessel, detailed in Figure 5.9.4. Unfortunately there was not enough time to test this *ex-situ* reduction vessel during this project, this would be an interesting area for future investigation.

Improvements in catalyst activation procedures are necessary before future work can yield the benefits of using the combination of the elevated pressure reactor and the promise of improved selectivity to the formation of *cis*-2-butene-1,4-diol from 2-butyne-1,4-diol while using supported copper catalysts.

5.9.2 SUMMARY OF THE HYDROGENATION OF 2-BUTYNE-1,4-DIOL EMPLOYING THE 9.1% Cu/SiO_2 CATALYST

- There is high selectivity towards *cis*-2-butene-1,4-diol formation (Figure 5.9.1) and butane-1,4-diol formation (Figure 5.9.2), with it being consistently over 98% when the 9.1% Cu/SiO_2 catalyst is employed.

- The 9.1% Cu/SiO_2 catalyst produces fewer "side products" than the equivalent 1% palladium catalyst reactions.

- There is no formation of iso-propoxytetrahydrofuran, or any other products that have not been observed in other reactions.

- The reaction rate is considerably slower when the 9.1% Cu/SiO_2 catalyst is employed with the ambient pressure reaction vessel.

- There was no observed reaction in the elevated pressure reaction vessel when the 9.1% Cu/SiO_2 catalyst was employed, due to problems with the catalyst reduction.

- Further work is required to achieve reduction of the 9.1% Cu/SiO_2 catalyst, and hydrogenation in the elevated pressure reaction vessel, a new *ex-situ* reduction vessel has been designed and built for this.

5.10 USING WATER AS A REPLACEMENT SOLVENT

This section summarises reactions that were conducted at ambient and elevated pressure using two 1% Pd/C catalyst with distilled water being used as a replacement solvent. Up to this point this project has concerned the selective hydrogenation of 2-butyne-1,4-diol to *cis*-2-butene-1,4-diol employing propan-2-ol as the reaction solvent, with a variety of supported palladium catalysts. There have studies detailed in the literature that have investigated the selective hydrogenation of 2-butyne-1,4-diol using water as the reaction solvent [9, 20, 21, 22, 23, 24, 37]. Chaudhari *et al* [22] has reported the formation of products such as γ-hydroxybutyraldehyde, *n*-butyraldehyde and an acetal, when water has been used as the reaction solvent for the hydrogenation of 2-butyne-1,4-diol. This series of experiments aims to ascertain whether the reaction solvent can have a significant effect of the reaction rate, the products produced, and product distributions observed.

Using distilled water as the reaction solvent, it is unlikely that iso-propoxytetrahydrofuran will be produced, as there is no easy route to the formation of the require propan-2-ol. There is the possibility of other side products being formed that would not be found when using the 1% Pd/C catalyst employing propan-2-ol as the reaction solvent. This section can be divided into two parts, i) ambient pressure reactions employing distilled water as a replacement solvent (Figures 5.10.1 and 5.10.2), and ii) an elevated pressure reaction employing distilled water as a replacement solvent (Figure 5.10.3).

i) Ambient Pressure Reactions

Tables 5.10.1 and 5.10.2 detail a summary of the reaction data, and Figures 5.10.1 and 5.10.2 shows reaction profiles for ambient pressure reactions employing the 1% Pd/C catalyst and distilled water as a replacement solvent with 2-butyne-1,4-diol and *cis*-2-butene-1,4-diol respectively.

The experimental procedure for Figures 5.10.1 and 5.10.2 was the same as that detailed in Section 3.5 for an ambient pressure reaction that employed a programmed *in-situ* reduction of the catalyst (reduction of catalyst in the gas phase), with the exception that distilled water was used as the reaction solvent. Figure 5.10.1 reached a conversion of the 2-butyne-1,4-diol of 95.69% in 1410 minutes. The initial selectivity towards the formation of *cis*-2-butene-1,4-diol quite low (in the order of 50%), the selectivity did reach 98.46% by a conversion of 79.46%. Figure 5.10.2 reached a conversion of the *cis*-2-butene-1,4-diol of 47.83% in 750 minutes. A selectivity towards the formation of butane-1,4-diol of 98% was maintained until a conversion 47.83%, this selectivity is significantly higher than had been previously observed Section 5.2 when propan-2-ol had been employed as the reaction solvent.

In both Figures 5.10.1 and 5.10.2 there was no formation of *cis* or *trans*-crotyl alcohol, 3-buten-1-ol or iso-propoxytetrahydrofuran observed during the course of the reaction, these products would normally be observed when using 2-butyne-1,4-diol or *cis*-2-butene-1,4-diol and the 1% Pd/C catalyst with propan-2-ol. In Figures 5.10.1 and 5.10.2 there was formation of hydroxy-tetrahydrofuran. This had previously been observed when the 1% Pd/Al_2O_3 catalyst (nitrate precursor) was employed. The formation of hydroxy-tetrahydrofuran is consistent with the postulated reaction mechanism detailed in Chapter 6.

The rate of hydrogenation for Figure 5.10.1 and 5.10.2 were 9.19×10^{-6} and 8.18×10^{-6} moles/l/s/g catalyst, these rates are approximately half of the equivalent rates for experiments in Section 5.2 that employed propan-2-ol as

the reaction solvent. The mass balances for Figures 5.10.1 and 5.10.2 were 98.97% and 99.86% respectively, these compare well with the mass balances for similar reactions in Section 5.2 that employed propan-2-ol as the reaction solvent (their mass balances were in the order of 70%). The mass balance profiles for Figures 5.10.1 and 5.10.2 can be seen in Figure 5.10.4 a) and 5.10.4 b) respectively.

ii) Elevated Pressure Reaction

Table 5.10.3 details a summary of the reaction data, and Figures 5.10.3 shows reaction profiles for an elevated pressure reaction employing the 1% Pd/C catalyst and distilled water as a replacement solvent with 2-butyne-1,4-diol.

The experimental procedure was the same as that detailed in Section 3.6 for an ambient pressure reaction that employs the 1% Pd/C catalyst that employed programmed ex-situ reduction of the catalyst, with the exception of distilled water being used as the reaction solvent. This experiment reached a conversion of 2-butyne-1,4-diol of 96.18% in 300 minutes. As above, this was lower than the amount of conversion that would be seen in an elevated pressure reaction employing the 1% Pd/C catalyst over a shorter period of time. It only takes approximately 120 minutes to hydrogenate all the 2-butyne-1,4-diol when the 1% Pd/C catalyst is employed with propan-2-ol, as above the change of the reaction solvent has approximately doubled the amount of time required to fully hydrogenate all the 2-butyne-1,4-diol.

There was a selectivity in the order of 90% towards the formation of *cis*-2-butene-1,4-diol until 89.50% conversion. As in Figures 5.10.1 and 5.10.2 there was no formation of *cis* or *trans*-crotyl alcohol, 3-buten-1-ol or iso-propoxytetrahydrofuran observed during the course of the reaction, there was the formation of hydroxy-tetrahydrofuran in this reaction as above.

The rate of hydrogenation of 2-butyne-1,4-diol around half that observed in a similar reaction that employed the 1% Pd/C catalyst and propan-2-ol, $1.43x10^{-5}$ as opposed to $3.07x10^{-5}$ moles/l//s/g catalyst. The mass balance at the end of the reaction was 97.27%. The mass balance profile for Figure 5.10.3 can be seem in Figure 5.10.4 c).

Table 5.10.1 Ambient pressure reaction employing the 1% Pd/C catalyst and distilled water

Time (minutes)	Butyne-1,4-diol (moles/l)	Butene-1,4-diol (moles/l)	Butane-1,4-diol (moles/l)	Butanol (moles/l)	Hydroxy-thf (moles/l)	Conversion (%)	Selectivity (%)
0	0.2121	0	0	0	0	0	0
30	0.2045	0.0026	0	0	0	3.56	34.80
90	0.1864	0.0063	0	0	0	12.12	24.68
150	0.1816	0.0117	0.0028	0	0	14.39	38.47
210	0.1744	0.0210	0.0032	0	0	17.75	55.66
1170	0.0436	0.1659	0.0109	0	0	79.46	98.46
1290	0.0246	0.1892	0.0136	0	0	88.40	100.89
1410	0.0091	0.1775	0.0157	0	0	95.69	87.45
1470	0.0076	0.1717	0.0147	0	0.0001	96.44	83.97
1530	0.0063	0.1685	0.0191	0.0001	0.0002	97.03	81.90
1570	0.0062	0.1669	0.0231	0.0002	0.0003	97.06	81.07
1645	0.0062	0.1624	0.0268	0.0002	0.0004	97.06	78.87
2785	0.0062	0.1081	0.0962	0.0002	0.0005	97.07	52.52
2895	0.0062	0.0945	0.1083	0.0003	0.0006	97.07	45.91

Figure 5.10.1 Reaction profile for ambient pressure reaction employing the 1% Pd/C catalyst and distilled water

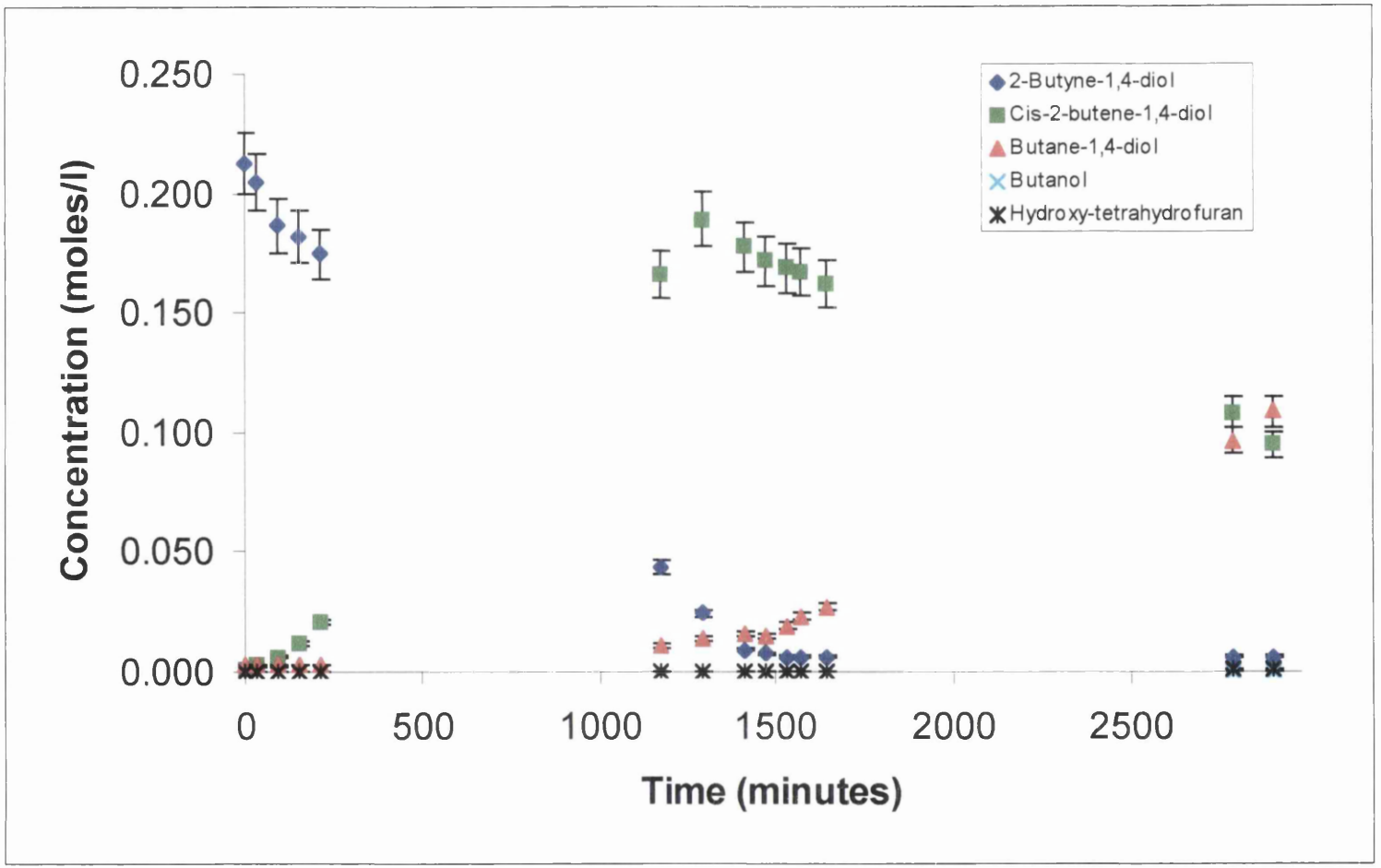


Table 5.10.2 Ambient pressure reaction employing the 1% Pd/C catalyst and distilled water with *cis*-2-butene-1,4-diol

Time (minutes)	Butene-1,4-diol (moles/l)	Butane-1,4-diol (moles/l)	Butanol (moles/l)	Hydroxy-thf (moles/l)	Conversion (%)	Selectivity (%)
0	0.2112	0	0	0	0	0
15	0.2055	0.0057	0	0	2.70	99.81
45	0.2020	0.0091	0	0	4.37	98.96
75	0.1921	0.0180	0	0	9.05	94.05
105	0.1875	0.0217	0	0	11.24	91.23
120	0.1818	0.0269	0	0	13.92	91.62
135	0.1800	0.0288	0	0	14.79	92.09
150	0.1754	0.0357	0	0	16.98	99.70
180	0.1733	0.0373	0	0	17.95	98.41
210	0.1695	0.0415	0	0.0001	19.78	99.35
225	0.1679	0.0422	0	0.0002	20.51	97.48
670	0.1221	0.0828	0.0001	0.0003	42.19	92.92
720	0.1142	0.0962	0.0001	0.0003	45.92	99.19
750	0.1102	0.1001	0.0002	0.0004	47.83	99.11

Figure 5.10.2 Reaction profile for an ambient pressure reaction employing the 1% Pd/C catalyst and distilled water with *cis*-2-butene-1,4-diol

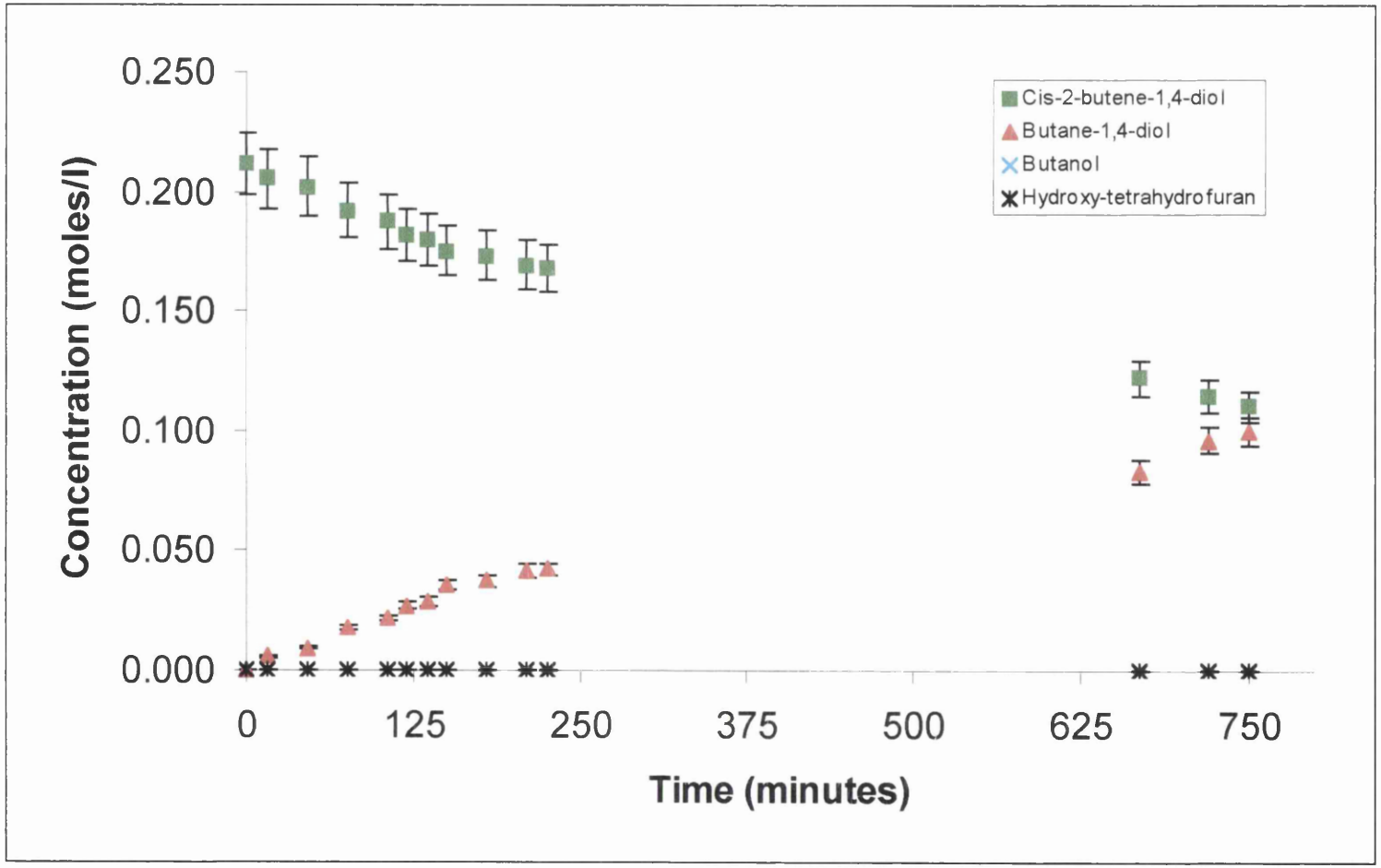


Table 5.10.3 Elevated pressure reaction employing the 1% Pd/C catalyst and distilled water

Time (minutes)	Butyne-1,4-diol (moles/l)	Butene-1,4-diol (moles/l)	Butane-1,4-diol (moles/l)	Butanol (moles/l)	Hydroxy-thf (moles/l)	Conversion (%)	Selectivity (%)
0	0.2381	0	0	0	0	0	0
30	0.2032	0.0290	0	0	0	14.66	83.10
60	0.1853	0.0471	0	0	0	22.18	89.21
90	0.1124	0.0973	0.0090	0	0.0041	52.79	77.41
120	0.0812	0.1434	0.0108	0	0.0050	65.90	91.40
150	0.0479	0.2112	0.0183	0	0.0073	79.88	111.04
180	0.0250	0.1491	0.0250	0	0.0090	89.50	69.97
240	0.0155	0.0674	0.0668	0	0.0125	93.49	30.28
300	0.0091	0.0112	0.0857	0.0032	0.0143	96.18	4.89
540	0.0087	0.0020	0.0921	0.0151	0.0440	96.35	0.87
600	0.0080	0.0019	0.1062	0.0315	0.0613	96.64	0.83
1440	0.0078	0.0018	0.1064	0.0464	0.0683	96.72	0.78
1560	0.0071	0.0018	0.1072	0.0473	0.0682	97.02	0.78

Figure 5.10.3 Reaction profile for an elevated pressure reaction employing the 1% Pd/C catalyst and distilled water

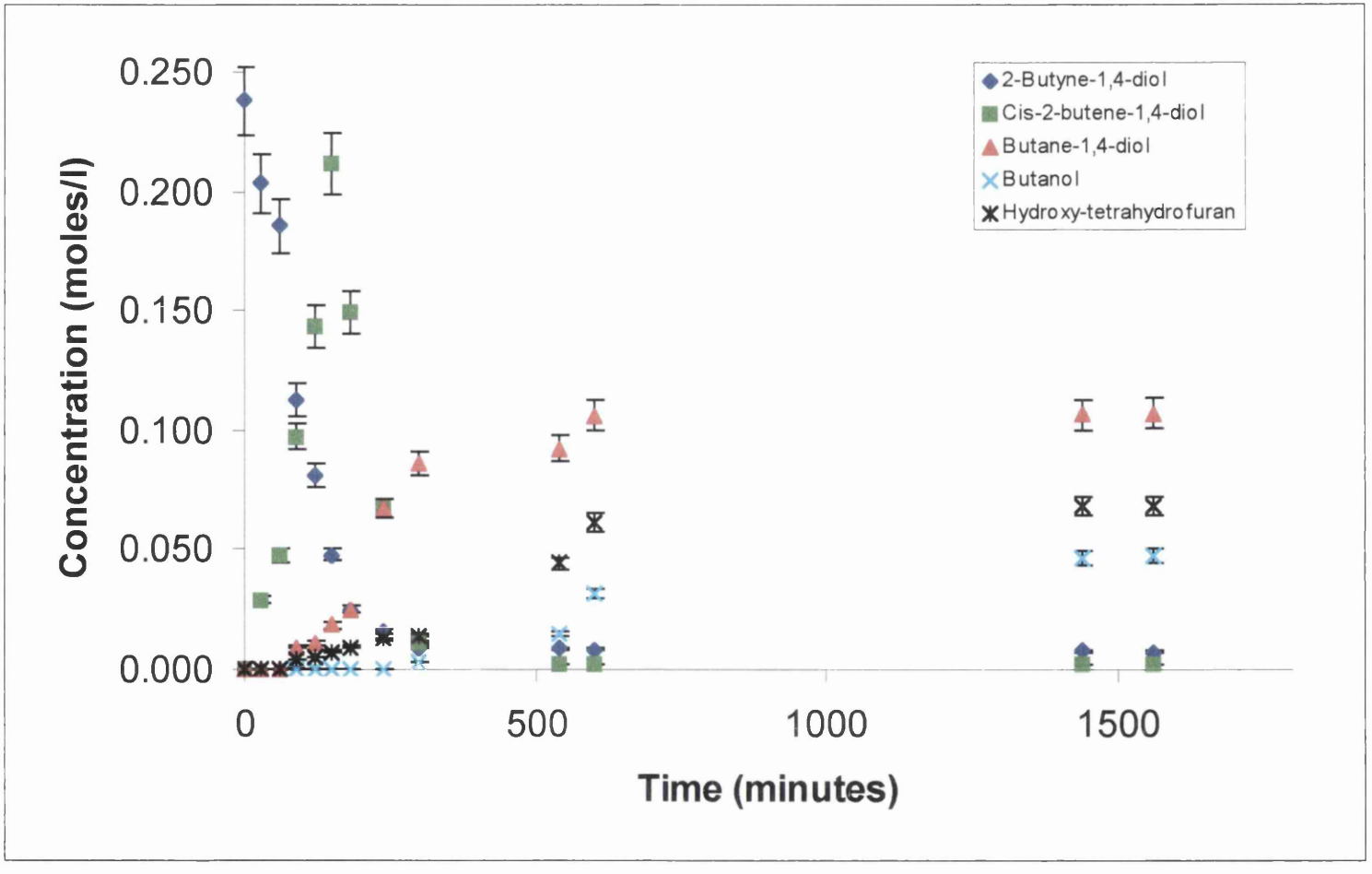
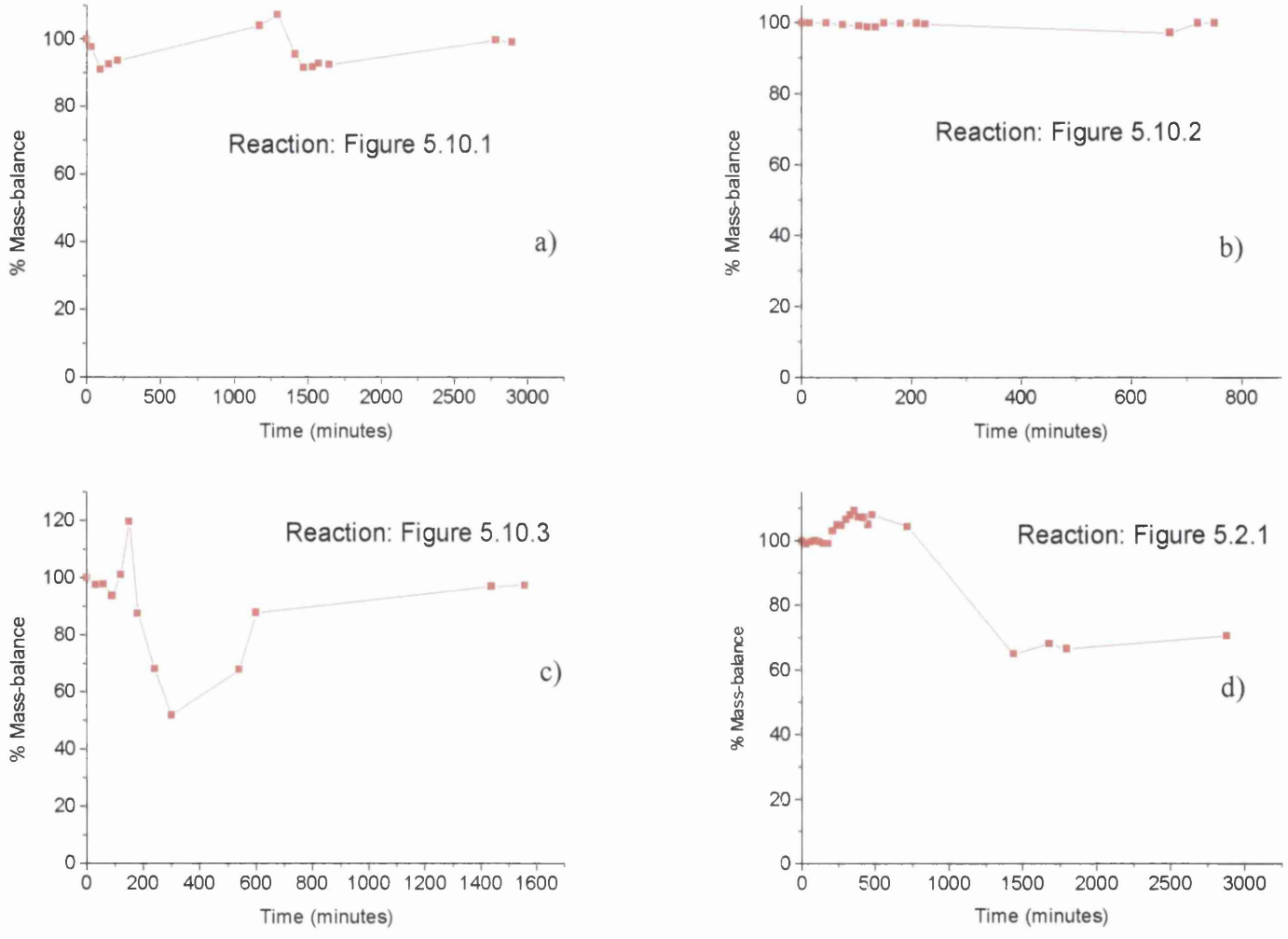


Figure 5.10.4 Mass-balances for reactions in Section 5.10 and Figure 5.2.1 from Section 5.2



5.10.1 Discussion for using water as a replacement solvent

All the ambient and elevated pressure reactions in this section do not show a number of products that would that were observed in the reactions that have used propan-2-ol as the reactions solvent. The products that do not appear when distilled water is used instead of propan-2-ol are 3-buten-1-ol, *cis* and *trans*-crotyl alcohol and iso-propoxytetrahydrofuran. Instead, the iso-propoxytetrahydrofuran is replaced with hydroxy-tetrahydrofuran. The use of distilled water as the reaction solvent has reduced the number of "side products". The major product at the end of all the reactions detailed in this section is butane-1-,4-diol instead of iso-propoxytetrahydrofuran as in the equivalent reactions that used propan-2-ol as the reaction solvent, detailed in Section 5.2. Other solvent such as hexane and butanol have also be tried, 2-butyne-1,4-diol was not soluble in hexane (2-butyne-1,4-diol requires a relatively polar solvent), a sample plot for a reaction that employed butanol as the reaction solvent can be seen in Section 5.11. The solvent seems to play a role in the final product distribution of the products formed.

Hydroxy-tetrahydrofuran is produced in the place of iso-propoxytetrahydrofuran due to the fact that there is no propan-2-ol present in the in the reaction vessel. The precursor to the formation of iso-propoxytetrahydrofuran is still present at the catalyst surface, but instead of being able to have a concerted ring closure with a propoxy group, the hydroxyl is present instead. The presence of the hydroxyl group leads to the formation of the hydroxy-tetrahydrofuran. The formation of hydroxy-tetrahydrofuran is completely consistent with the reaction mechanism as detailed in Chapter 6.

By comparing both the ambient (Figure 5.10.1) and elevated (Figure 5.10.3) pressure experiments in this section that detail the selective hydrogenation of 2-butyne-1,4-diol, it can be seen that as with the equivalent reactions that employ propan-2-ol as the reaction solvent (Section 5.2), the increase in pressure between the ambient and elevated pressure reactions does not have a

significant effect on the final product distributions (taking into account that the ambient pressure reactions does not reach 200% conversion in the timeframe of the reaction profile covers).

The rate of hydrogenation of *cis*-2-butene-1,4-diol for the ambient pressure reaction (Figure 5.10.2) that employed distilled water as the reaction solvent was 8.18×10^{-6} moles/l/s/g catalyst respectively. This rate compares quite well with the rate of hydrogenation of 2-butyne-1,4-diol in the ambient and elevated pressure reactions, 9.19×10^{-6} and 1.43×10^{-5} moles/l/s/g catalyst for the elevated pressure reaction. The rate of hydrogenation of *cis*-2-butene-1,4-diol in the ambient pressure reactions is slower than the rates for the hydrogenation of 2-butyne-1,4-diol due to the different adsorption energies the two species have at the catalyst surface.

The elevated pressure reaction (Figure 5.10.3) detailed in this section for the selective hydrogenation of 2-butyne-1,4-diol displayed an increased rate of reaction when compared the ambient pressure reactions in this section. This in is not unexpected, the increase in reaction rate with increased pressure has been observed in Section 5.2.

As with the equivalent reactions that employ propan-2-ol as a reaction solvent, there is relatively little hydrogenation of *cis*-2-butene-1,4-diol when there is still 2-butyne-1,4-diol available in the reaction vessel for hydrogenation in the ambient and elevated pressure reactions. As with the reactions detailed in Section 5.2, there is competitive adsorption between 2-butyne-1,4-diol and *cis*-2-butene-1,4-diol on the surface of the catalyst in both the ambient and elevated pressure reactions (with 2-butyne-1,4-diol dominating because of its relatively higher adsorption coefficient), preventing access to active sites for *cis*-2-butene-1,4-diol when there is still 2-butyne-1,4-diol present in the reaction solution. There is also competition with water molecules for the adsorption sites.

Comparing the selectivity for the hydrogenation of 2-butyne-1,4-diol in the ambient and elevated pressure reactions, with the selectivity of the

hydrogenation of *cis*-2-butene-1,4-diol in the ambient and elevated pressure reactions, illustrates an interesting point that is not mirrored by the reactions that employ propan-2-ol as the reaction solvent. After the initial period the selectivity to the formation of *cis*-2-butene-1,4-diol formation is over 90% in both the ambient and elevated pressure reactions, as with the reactions in Section 5.2 that use propan-2-ol as the reaction solvent. Unlike the equivalent reactions in Section 5.2, however, the selectivity towards the formation of butane-1,4-diol for the hydrogenation of *cis*-2-butene-1,4-diol in both the ambient and elevated pressure reaction vessels is in the order of 90%. The significantly higher selectivity towards the formation of butane-1,4-diol in both the ambient and elevated pressure reactions illustrates that when distilled water is used as the reaction solvent the ability of the adsorbed *cis*-2-butene-1,4-diol species to be converted to the other "side products" has been reduced. This is reflected in the (far) higher selectivity during the second stage of the reaction, and the more limited range of products that are observed in the product distributions, and the increased amount of butane-1,4-diol that is formed by the end of the reaction. When distilled water is employed as the reaction solvent there is a different range of reaction products in the second stage of the hydrogenation process. Presumably the presence of the water at the Pd surface impedes these side reactions and the direct hydrogenation route is favoured.

The rates of hydrogenation for the ambient and elevated pressure reactions in this section for 2-butyne-1,4-diol and *cis*-2-butene-1,4-diol are uniformly around half the rates of the equivalent reactions in Section 5.2. This is due to competition on the catalyst surface for adsorption between distilled water and 2-butyne-1,4-diol (and/or *cis*-2-butene-1,4-diol), this competition not only slows the rate of hydrogenation but also helps prevent the reactions of the intermediate species (see Chapter 6) that can go on to form butane and butene, with their formation being the main reason for the mass imbalance experienced in the reactions in Sections 5.2 and 5.8 when employing propan-2-ol with the 1% Pd/C catalyst. It has been reported in the literature that the "side products" come form acid hydrogenolysis [9, 20, 22, 37] which can be enhanced under acidic conditions. The relatively more acidic reaction solution

in the experiments in the section (around pH 2.4) should produce more side products when compared to the experiments in Section 5.2 (around pH 5.2), but more importantly more butane and butene leading to a less complete mass balance. This is not the case because the rate of reaction is retarded by the presence of adsorbed water on the catalyst surface, enabling the adsorbed reaction intermediates to desorb from the catalyst surface before they can lose both hydroxyl groups to become butane and butene, certainly retention of the mass balance in consistent with the product distribution that is observed in the experiments in this section. The reactions detailed in this section seem to be displaying the opposite behaviour than that suggested by the literature references above.

Using distilled water as the reaction solvent we sacrifice reaction rate, but gain increased selectivity during the first stage of the reaction to *cis*-2-butene-1,4-diol, and greatly increased selectivity towards butane-1,4-diol during the second stage of the reaction. The use of distilled water also reduces the amount of "side products" that are found in the final product distribution.

The formation of hydroxy-tetrahydrofuran has important implications for the overall reaction mechanism, it could possible to extend this facet of the overall reaction mechanism to produce other substituted furans, simply by varying the reaction solvent. We have seen evidence from the reactions that use the 1% Pd/Al_2O_3 catalyst (nitrate precursor) that we can produce different substituted furans by varying the catalyst support. In the case of the 1% Pd/Al_2O_3 catalyst (nitrate precursor) the presence of the hydroxyl groups on the support material lead to the formation of hydroxy-tetrahydrofuran. Future work could further exploit the ability to form other substituted furans, in a catalytic manner as has been detailed in the reactions here. Substituted furans have more commercial value than the other alcohol species that are normally produced in this type of catalytic reaction.

5.10.2 SUMMARY FOR WATER AS A REPLACEMENT SOLVENT

- Fewer "side products" are produced when water is employed as the reaction solvent, there was no formation of *cis* or *trans*-crotyl alcohol or 3-buten-1-ol.

- Hydroxy-tetrahydrofuran was produced in the place of iso-propoxytetrahydrofuran due to the fact that there was no propan-2-ol present to react with the iso-propoxytetrahydrofuran precursor. This opens the possibility of being able to produce different substituted furans by varying the reaction solvent.

- For Figures 5.10.1 and 5.10.3 the selectivity towards butane-1,4-diol formation during the second stage of the reaction was greatly improved when compared to the reactions in Section 5.2, the selectivity towards butane-1,4-diol formation in Figure 5.10.2 showed a similar improvement.

- The mass balance when distilled water was employed as the reaction solvent was more complete than when propan-2-ol was used as the reaction solvent. Distilled water seems to inhibit some of the hydrogenolysis that can lead to the formation of butene and butane, which can have a detrimental effect of the overall mass balance.

- There is competition between water and 2-butyne-1,4-diol (and/or *cis*-2-butene-1,4-diol) on the catalyst surface, leading to a reduced rate of hydrogenation, and no discernible formation of butane and butene.

- Acid hydrolysis has been reported in the literature as the probable source for the reaction pathways that lead to the formation of the "side-products". This seems to be in disagreement with the experimental observations in this section.

5.11 ISO-PROPOXYTETRAHYDROFURAN PURIFICATION, CALIBRTION AND AN INITIAL BUTANOL TEST REACTION

It was originally thought that iso-propoxytetrahydrofuran was something like butyrolacetone, after an extensive literature search a paper was found that detailed the formation of iso-propoxytetrahydrofuran from 3-buten-1-ol [38]. This paper describes the formation of iso-propoxytetrahydrofuran but under oxidative conditions, the reverse of the conditions that are present in the reaction vessel during the selective hydrogenation of 2-butyne-1,4-diol. ^{1}H NMR and MS were used to confirm the presence of iso-propoxytetrahydrofuran in the final reaction solution. This section can be split into two parts, i) purification and calibration of iso-propoxytetrahydrofuran, and ii) an initial butanol test reaction.

i) Purification and calibration of iso-propoxytetrahydrofuran

This part of the section details how iso-propoxytetrahydrofuran was further purified after it had been confirmed in the sample, so that a calibration curve could be constructed from standard solutions of iso-propoxytetrahydrofuran. Figure 5.11.1 shows a standard ^{1}H NMR spectrum that was obtained by using the method outlined in Section 3.8. The spectrum detailed a solution that has around a 40% concentration of iso-propoxytetrahydrofuran. The spectrum employs the same naming convention as outlined in Chapter 6, Figure 6.4.1 and Table 6.4.1 can be used to assign the peaks in Figure 5.11.1 (it should be noted that when the spectrum in Figure 5.11.1 was conducted the NMR required a service, this along with concentration differences accounts for any drift between the spectra in Chapter 6 and Figure 5.11.1).

To calibrate the GC for iso-propoxytetrahydrofuran the solution had to be further purified. To achieve this, the solution was decanted in approximately 0.2ml quantities in a sample vial. To reduce the solvent content a slow flow of helium was employed to drive the solvent off (in the case of this sample it was

mostly propan-2-ol with a little butanol). The procedure was employed to get enough relatively pure iso-propoxytetrahydrofuran to allow for GC calibration. GC analysis of the sample was conducted to check the purity, diluted in both propan-2-ol and butanol to assess the amount of butanol and propan-2-ol left in the purified sample. Using this method it was possible to produce a sample that was 95.85% iso-propoxytetrahydrofuran.

Calibration tests were conducted on the newly purified sample by producing a set of known mass standards (0.2g/10ml) with the purified sample diluted both in propan-2-ol and butanol, this way the actual concentration of iso-propoxytetrahydrofuran in the standard solutions could be confirmed (and any of the other reaction products that were left in the purified sample could be assessed). A different calibration has subsequently been employed be Iain Duncanson, his method confirms the calibration curves produced for iso-propoxytetrahydrofuran from the method outlined above [10].

ii) Initial butanol test reaction

It has been stated in earlier sections that a solvent interaction between the reaction solvent and an adsorbed species present on the catalyst surface is responsible for the formation of the resultant furan species. Section 5.10 has illustrated that when distilled water was employed as the reaction solvent that hydroxy-tetrahydrofuran was produced. To examine if this was the case for other solvents, initial tests were conducted employing n-butanol as the reaction solvent. Figure 5.11.2 details a reaction profile for a reaction that employed butanol as the reaction solvent, Figure 5.11.3 is a mass-spectrum for the furan compound that was produced in the reaction, the compound was butoxy-tetrahydrofuran, confirmed by ^{1}H NMR in combination with the mass-spectrum. The main feature of the mass-spectrum is the main peak at 71, corresponding to the furan ring. The peak at 144 indicates a molecular mass that would be consistent with butoxy-tetrahydrofuran. The mass-balance for this reaction was not considered as butanol is one of the reaction products, but

the initial reaction confirms the possibility of producing other furans simply by switching the reaction solvent.

Figure 5.11.1: ^{1}H NMR iso-propoxytetrahydrofuran purification spectra

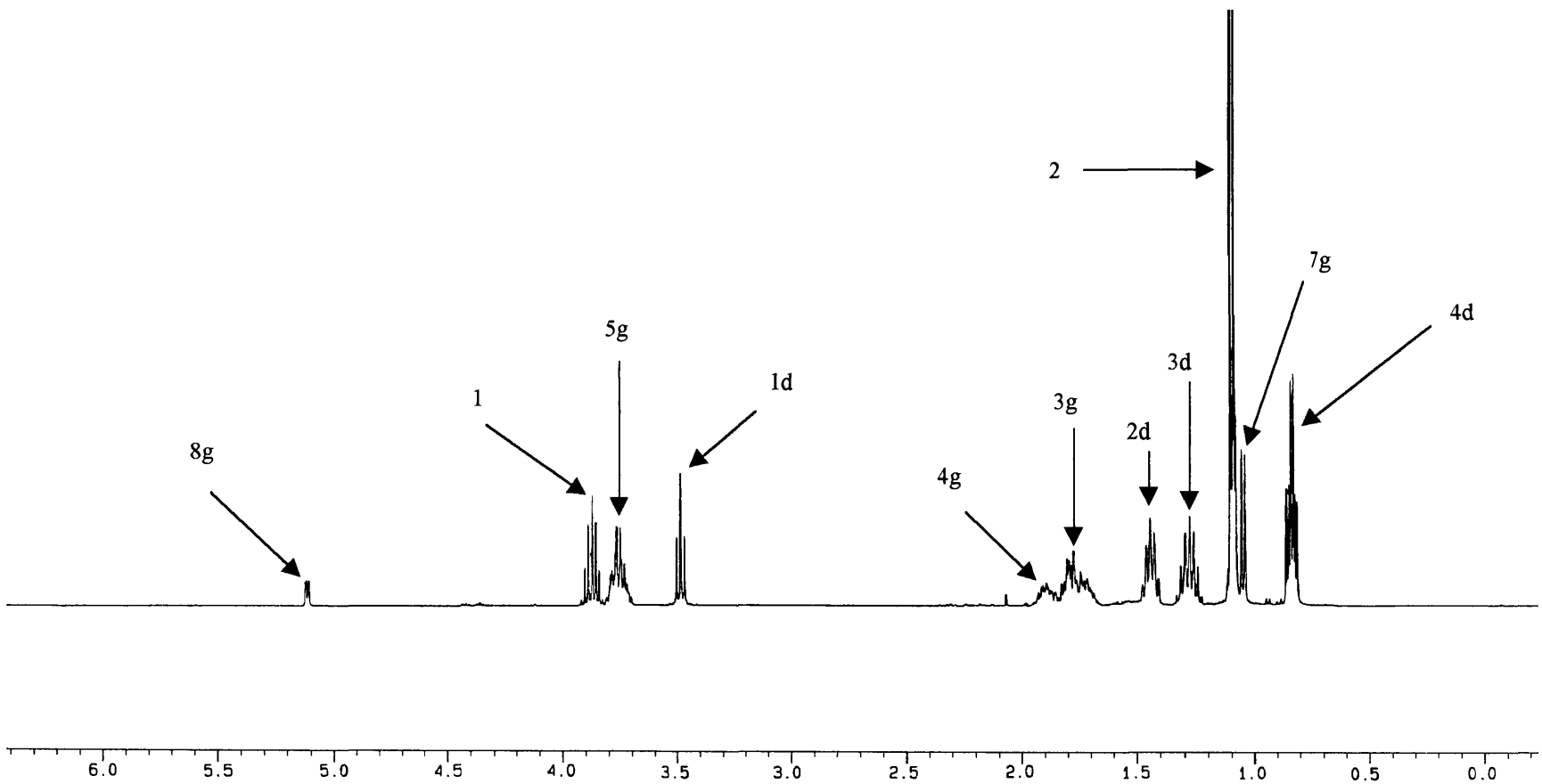


Figure 5.11.2: Reaction profile for an ambient pressure reaction employing butanol as the reaction solvent

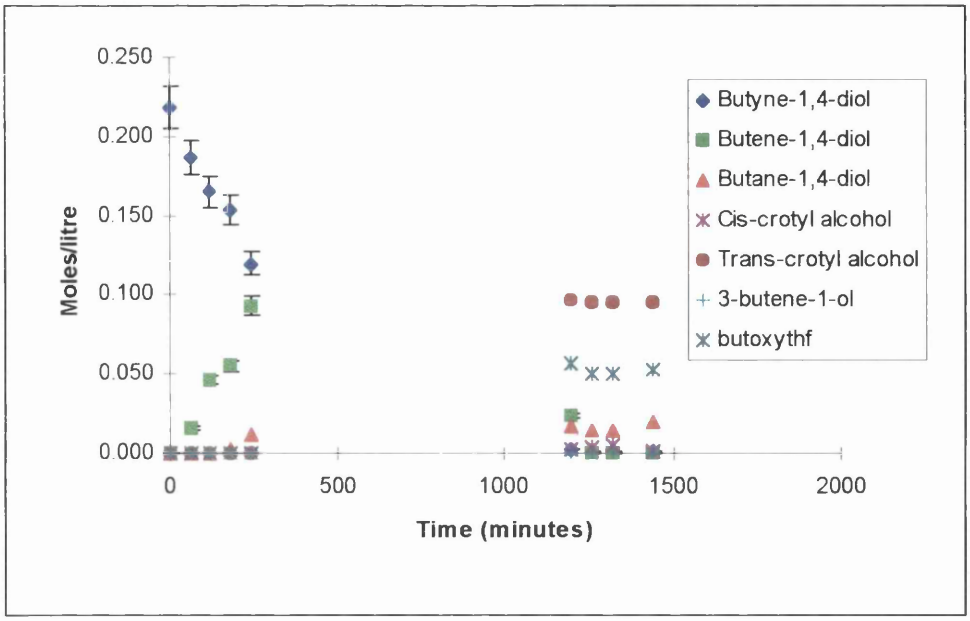
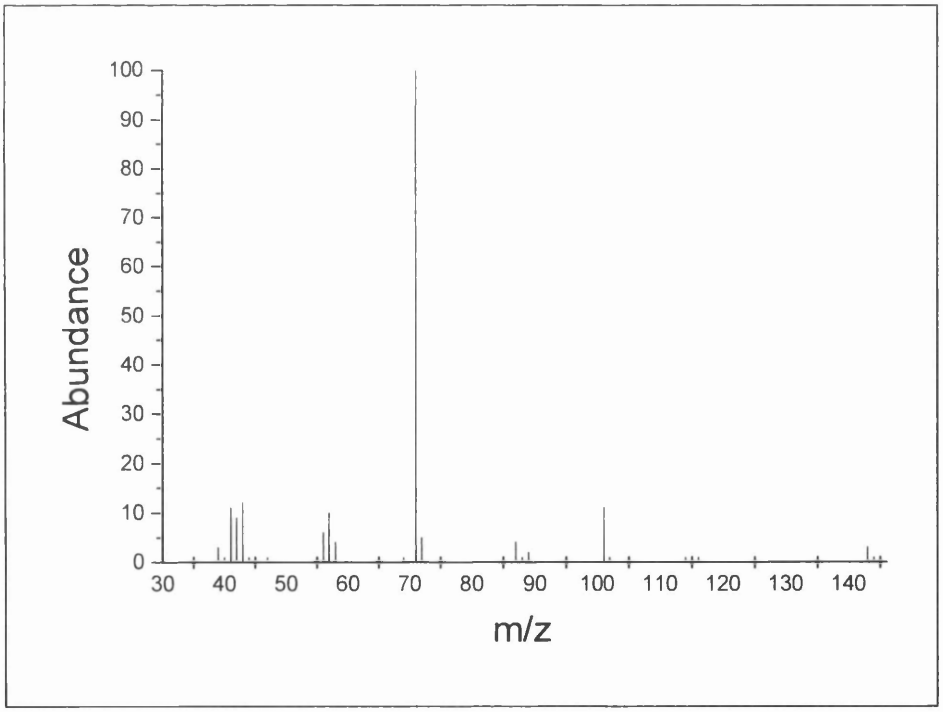


Figure 5.11.3: Mass-spectrum for butoxy-tetrahydrofuran



5.11.1 SUMMARY FOR SECTION 5.11

- Iso-propoxytetrahydrofuran was identified and confirmed using a combination of ^{1}H NMR and GC-MS.

- Iso-propoxytetrahydrofuran was further purified to 95.85% by carefully blowing the solvent off with a slow supply of Helium for calibration purposes.

- It has been shown that changing the reaction solvent will effect the furan that is produced, with distilled water hydroxy-tetrahydrofuran was produced, and with butanol butyoxy-tetrahydrofuran was produced.

5.12 ELEVATED PRESURE INVESTIGATION INTO POSSIBLE HOMOGENEOUS REACTIONS

This section summarises elevated pressure reactions that were conducted to investigate the possibility of homogeneous processes being responsible for the formation reaction products such as iso-propoxytetrahydrofuran, rather than through the processes on the catalyst surface. To investigate the possibility that the catalyst was not directly involved in the formation of iso-propoxytetrahydrofuran and that homogeneous processes such as hydroformylation [39, 40, 41, 42, 43, 44] could be responsible for its formation, a number of modified elevated pressure reactions were performed. It has been reported in the literature for the selective hydrogenation of 2-butyne-1,4-diol that no reaction (and hence no homogeneous reaction(s)) occurs under reaction conditions in the absence of the catalyst [20]. The experimental procedure for the testing of the possible homogeneous formation of the reaction products can be split into two parts.

The first part of the experimental procedure for these experiments was largely the same as that detailed in Section 3.6 for an elevated pressure reaction. The main difference being that when the initial 2-butyne-1,4-diol had all been hydrogenated, and there was no further reaction, a spike (0.227 molar *cis*-2-butene-1,4-diol in the case of homogeneous test 1 and 0.233 molar 2-butyne-1,4-diol in the case of homogeneous test 2, Figures 5.12.1 and 5.12.2 respectively) was added to the final reaction mixture. Reaction samples were taken periodically during this part of the experimental procedure, and analysed as detailed in Section 3.9. Before the spike was added to the reaction mixture, the reaction slurry was collected for the elevated pressure reaction vessel and filtered. The filtration removed the bulk of the catalyst present, the remaining supernatant solution was then centrifuged for 5 minutes in $5cm^3$ centrifuge tubes to remove any of the particulates left in the reaction solution. All the catalyst had to be removed from the final reaction solution to ensure that there was no catalyst present that could contribute to the formation of any of the products, for the second part of the experiment.

The second part of the experimental procedure involved the introduction of a selected spike of either 2-butyne-1,4-diol (for homogeneous test experiment 2) or *cis*-2-butene-1,4-diol (for homogeneous test experiment 1) to a nominal concentration of 20g/l. Once the spike had been added to the filtered reaction solution (and all the spike material had been dissolved) a sample of the newly spiked reaction solution was taken and analysed by GC (that is the 1440 minute sample in both of the reaction profiles for this section). The spiked solution was then reintroduced into the elevated pressure reaction vessel and degassed for 30 minutes with a stream of N_2 gas. The gas was then changed to H_2, the scavenger was then closed and the elevated pressure reaction vessel was then allowed to reaction pressure. The experiment was left to continue under standard elevated pressure reaction conditions, with samples taken periodically to investigate if there was any evidence of homogeneous processes, leading to the formation of iso-propoxytetrahydrofuran.

If no further reaction occurred then the relative composition of the spiked reaction solution should remain the same at the end of the reaction, as it was when it had been spiked before the reintroduction of the solution into the reaction vessel. If there was evidence of the relative composition of the spiked solution changing when their was no catalyst present, and there was an increase in the amount of iso-propoxytetrahydrofuran present in the spiked solution, then the formation of iso-propoxytetrahydrofuran could be attributed to homogeneous processes. Figures 5.12.1 and 5.12.2 show the reaction profiles for the homogeneous test reactions that had a *cis*-2-butene-1,4-diol and 2-butyne-1,4-diol spike in them respectively. The summary table detailing the number of moles for each species present can be seen for the *cis*-2-butene-1,4-diol spike and the 2-butyne-1,4-diol spike in Tables 5.12.1 and 5.12.2 respectively.

Table 5.12.1: Elevated pressure reaction employing the 1% Pd/C catalyst to test for homogeneous reaction (with *cis*-2-butene-1,4-diol spike)

Time (minutes)	Butyne-1,4-diol (moles/l)	Butene-1,4-diol (moles/l)	Butane-1,4-diol (moles/l)	Butanol (moles/l)	*Cis*-crotyl alcohol (moles/l)	*T*-crotyl aicohol (moles/l)	3-buten-1-ol (moles/l)	Iso-propoxythf (moles/l)	1-(2-propanyox) (moles/l)
0	0.2461	0	0	0	0	0	0	0	0
60	0.1064	0.1214	0	0	0	0	0.0060	0.0012	0
120	0.0090	0.1454	0.0363	0.0153	0.0101	0.0078	0.0123	0.0199	0.0001
180	0.0075	0.0452	0.0391	0.0282	0.0146	0.0078	0.0120	0.0340	0.0003
240	0.0073	0.0021	0.0392	0.0291	0.0156	0.0081	0.0128	0.0438	0.0006
270	0.0073	0.0015	0.0420	0.0268	0.0153	0.0076	0.0116	0.0414	0.0006
1440	0.0073	0.2388	0.0438	0.0280	0.0155	0.0080	0.0121	0.0426	0.0006
1500	0.0073	0.2388	0.0436	0.0281	0.0152	0.0081	0.0123	0.0429	0.0006
1800	0.0073	0.2433	0.0447	0.0288	0.0155	0.0080	0.0122	0.0436	0.0006
2880	0.0073	0.2430	0.0447	0.0283	0.0153	0.0078	0.0118	0.0444	0.0006
3000	0.0073	0.2429	0.0409	0.0288	0.0152	0.0078	0.0121	0.0428	0.0006
3200	0.0073	0.2432	0.0412	0.0286	0.0152	0.0078	0.0123	0.0434	0.0006
3400	0.0073	0.2431	0.0410	0.0267	0.0154	0.0080	0.0124	0.0425	0.0006

Figure 5.12.1: Reaction profile for an elevated pressure reaction employing the 1% Pd/C catalyst to test for homogeneous reaction (with *cis*-2-butene-1,4-diol spike)

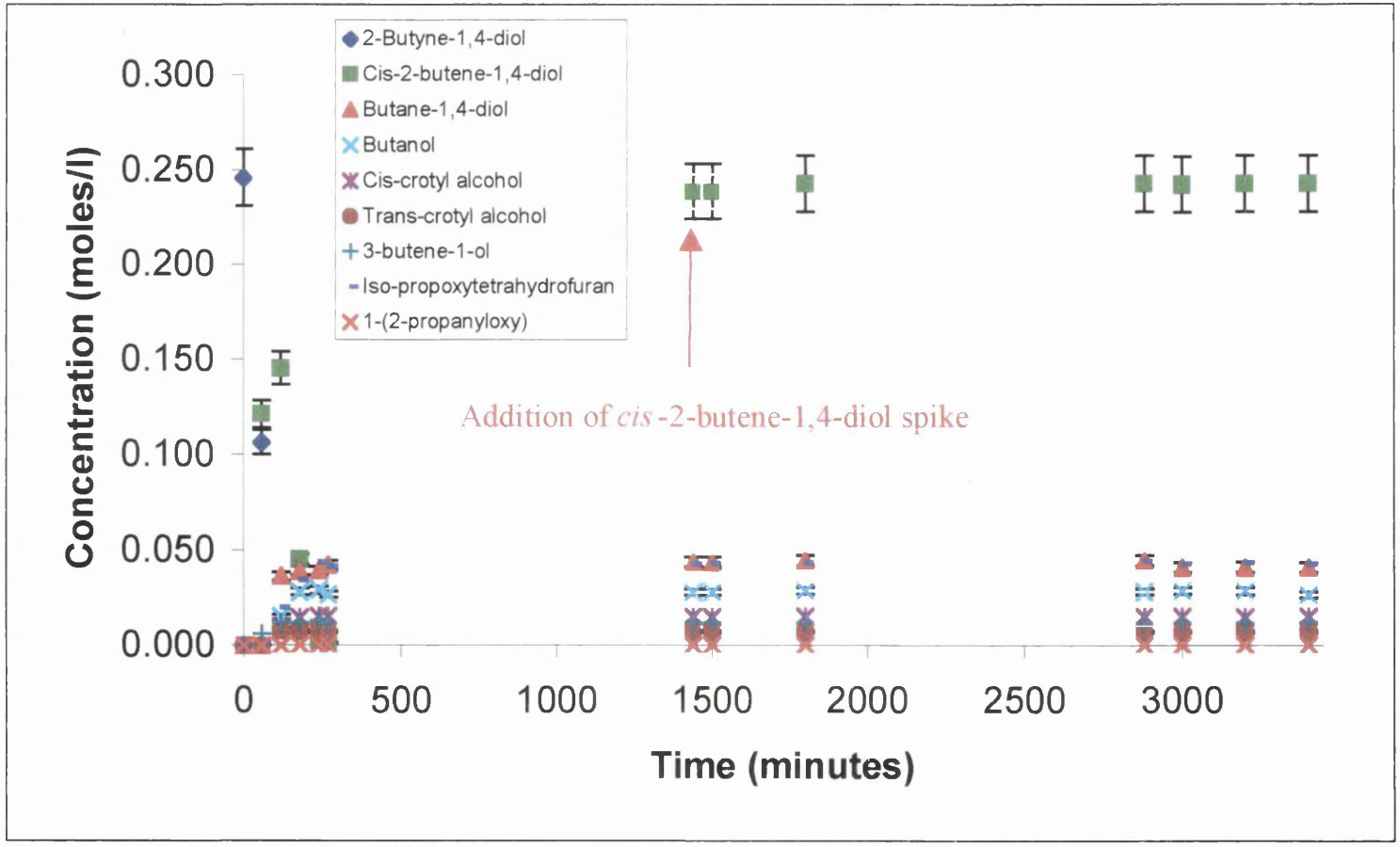
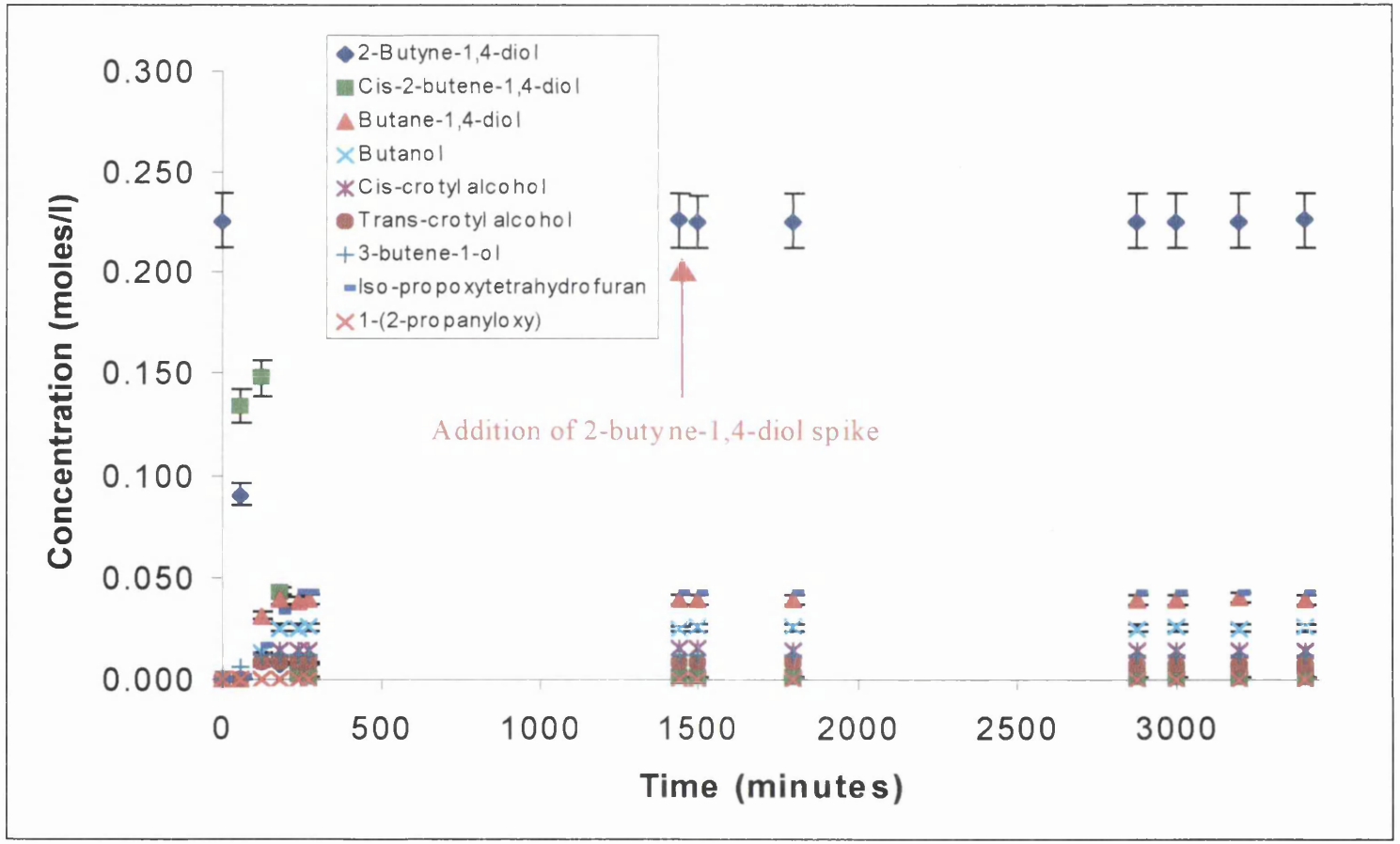


Table 5.12.2: Elevated pressure reaction employing the 1% Pd/C catalyst to test for homogeneous reaction (with 2-butyne-1,4-diol spike)

Time (minutes)	Butyne-1,4-diol (moles/l)	Butene-1,4-diol (moles/l)	Butane-1,4-diol (moles/l)	Butanol (moles/l)	*Cis*-crotyl alcohol (moles/l)	*T*-crotyl alcohol (moles/l)	3-buten-1-ol (moles/l)	Iso-propoxythf (moles/l)	1-(2-propanyox) (moles/l)
0	0.2259	0	0	0	0	0	0	0	0
60	0.0903	0.1339	0	0	0	0	0.0058	0.0011	0
120	0.0086	0.1479	0.0311	0.0128	0.0095	0.0080	0.0124	0.0170	0
180	0.0075	0.0427	0.0388	0.0254	0.0138	0.0078	0.0116	0.0330	0.0003
240	0.0074	0.0021	0.0383	0.0252	0.0146	0.0079	0.0117	0.0424	0.0005
270	0.0073	0.0015	0.0393	0.0255	0.0142	0.0079	0.0118	0.0422	0.0006
1440	0.2262	0.0015	0.0396	0.0247	0.0150	0.0081	0.0119	0.0425	0.0005
1500	0.2253	0.0015	0.0393	0.0256	0.0149	0.0079	0.0119	0.0428	0.0006
1800	0.2258	0.0015	0.0397	0.0257	0.0146	0.0078	0.0118	0.0429	0.0005
2880	0.2255	0.0015	0.0395	0.0255	0.0144	0.0076	0.0124	0.0423	0.0006
3000	0.2254	0.0015	0.0397	0.0257	0.0146	0.0073	0.0122	0.0423	0.0006
3200	0.2259	0.0015	0.0404	0.0254	0.0147	0.0075	0.0123	0.0423	0.0005
3400	0.2259	0.0015	0.0397	0.0256	0.0144	0.0076	0.0120	0.0424	0.0005

Figure 5.12.2: Reaction profile for an elevated pressure reaction employing the 1% Pd/C catalyst to test for homogeneous reaction (with 2-butyne-1,4-diol spike)



5.12.1 Discussion for elevated pressure investigation into possible homogeneous reactions

Both the *cis*-2-butene-1,4-diol and 2-butyne-1,4-diol spike homogeneous test reactions did not show any further reaction. This means that there was no catalyst left in the reaction solution after it had gone through both the filtration and centrifuge processes. If there had been any catalyst particulates present in the solution then there would have been evidence of reaction, you would expect to see at least some of the 2-butyne-1,4-diol would have been hydrogenated to form *cis*-2-butene-1,4-diol or in the case of the first homogeneous test reaction, some *cis*-2-butene-1,4-diol being converted to the other reaction products. This clearly was not the case with the concentrations of *cis*-2-butene-1,4-diol in the first homogeneous test reaction, and 2-butyne-1,4-diol in the second test reaction remaining the same (within experimental error) to the end of the reactions. There was also no significant change in any of the respective concentrations of any of the other products form the first part of the reaction. Species such as the *cis* and *trans*-crotyl alcohol, 3-buten-1-ol and the butanol did not get produced and/or converted when there was no catalyst present, therefore no reaction without the catalyst present.

If no reaction was observed, then iso-propoxytetrahydrofuran can not be produced from the reaction solution with no catalyst present. With no catalyst present, only a homogeneous type reaction would be possible, production of iso-propoxytetrahydrofuran in these conditions would give strong evidence that iso-propoxytetrahydrofuran is formed through homogeneous processes, there is no evidence to suggest that. Test experiments that have been conducted in the ambient and elevated pressure reaction vessels without the presence of catalyst at the start of the reaction have shown no formation of any reaction products. Iso-propoxytetrahydrofuran has been shown to be formed only when the catalyst is present, and in a heterogeneous type manner, the possibility of a homogeneous process being responsible for the production of the iso-propoxytetrahydrofuran when the catalyst is present can be discounted.

Chapter Six

RESULTS AND DISCUSSION PART (II)

6.1 INTRODUCTION

The purpose of this chapter is to try and use the spectroscopic methods of NMR and GC-MS to try and formulate a reaction mechanism that encompasses all the experimental observations made up to this point. Using the combination of H_2 and D_2 gas, ^1H NMR, ^{13}C NMR, GC and GC-MS analysis the reactions detailed here have been followed throughout their reaction profiles. By careful integration of all the spectroscopic and analytical elements, and the combination of previous experimental observations the aim is to propose a reaction mechanism that rationalises the mechanism in view of the experimental data. The earlier experiments, such as the competitive-adsorption, activation energies, order of reaction, the ambient and elevated pressure and the mono-substituted alkyne studies, all give insight into how the reaction pathways of the mechanism at the catalyst surface inter-relate.

A major goal of any mechanism is to explain the formation of iso-propoxytetrahydrofuran. Iso-propoxytetrahydrofuran is a product that was not expected to be formed when the reaction was first undertaken, yet it plays a significant role in the final reaction product distributions in all reactions involving 2-butyne-1,4-diol and the 1% palladium catalysts detailed in this thesis. There are "sister" products to iso-propoxytetrahydrofuran such as 1-(2-propanyloxy)-butan-1-ol and hydroxy-tetrahydrofuran. 1-(2-propanyloxy)-butan-1-ol is produced in small amounts in the elevated pressure reactions that employ the 1%Pd/C catalyst and instead of iso-propoxytetrahydrofuran in the mono-substituted reactions detailed in Section 5.8. Hydroxy-tetrahydrofuran is seen in the reactions that employ H_2O as a solvent and the ambient pressure reaction that employed the 1% Pd/Al_2O_3 (nitrate precursor) catalyst (through interaction of a reaction intermediate with hydroxyl groups on the support in the case of the 1% Pd/Al_2O_3 (nitrate precursor) catalyst). Like iso-propoxytetrahydrofuran these "sister" products would not be predicted under the reaction schemes described in the literature [1,2,3,4]. Although unexpected, the presence of these "sister" products in the product distributions should, with careful reasoning be able to be explained. It would be useful to

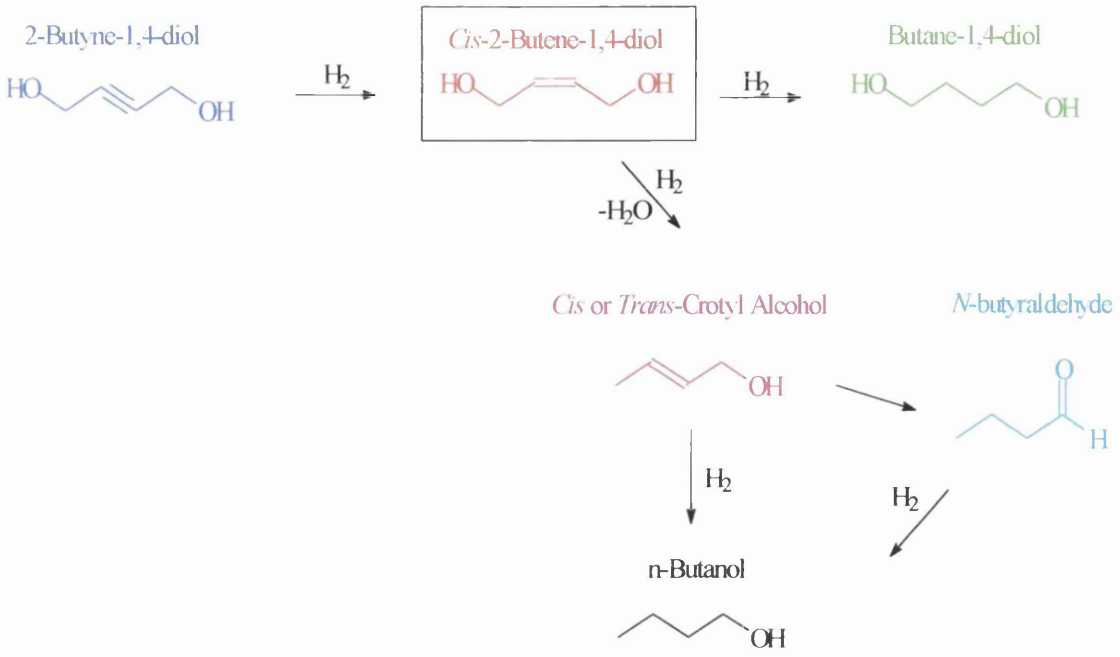
be able to tie these three similar, but chemically and physically disparate molecules together under a single, comprehensive reaction mechanism. A good understanding of the mechanisms that occur on the catalyst during the course of a reaction is always of use to a catalytic chemist. It is desirable, if possible to tailor the reaction chemistry to enhance the product distributions, so that more of the product(s) of choice is (are) produced.

The set of experiments that are detailed in this chapter have been designed to allow better understanding of how iso-propoxytetrahydrofuran and its sister products are formed. The experiments should also allow the various different reaction products such as *cis* and *trans*-crotyl alcohol, 3-buten-1-ol, *cis*-2-butene-1,4-diol and butane-1,4-diol to be brought together under one comprehensive mechanism. This detailed study will enable future optimisation of the reaction's conditions and catalyst to enable enhanced selectivity to the desired reaction products. The investment in time to conduct the experiments and formulate the reaction mechanism, will pay dividends in the increased understanding of the processes involved in the selective hydrogenation of 2-butyne-1,4-diol. The formation of a substituted furan could have some commercial benefits, and a simple catalytic route to the formation of furans is in contrast to a long, drawn out multistep organic synthesis. (see introduction)

6.2 DEVELOPMENT OF A REACTION MECHANISM

There are a few studies reported in the literature that propose a scheme for the selective hydrogenation of 2-butyne-1-,4-diol, using a supported ruthenium catalyst [3], and more interestingly using a supported palladium catalyst [1, 2, 4]. Winterbottom *et al* proposed a reaction scheme for the selective hydrogenation of 2-butyne-1,4-diol to *cis*-2-butene-1,4-diol using the supported palladium catalysts, detailing the side products that can be produced during the reaction, detailed in Figure 6.2.1 [1].

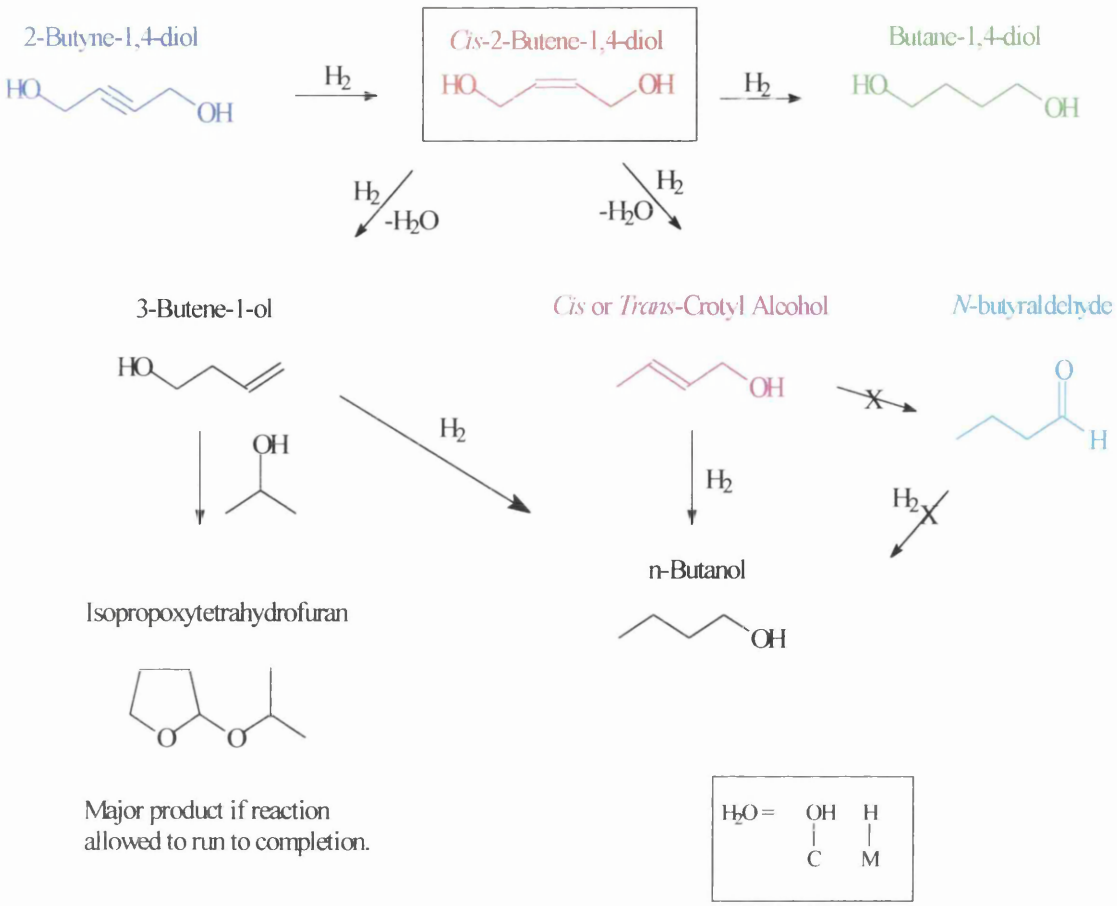
Figure 6.2.1 Proposed reaction scheme by Winterbottom *et al* [1]



Winterbottom *et al* reported that 2-butyne-1,4-diol could be selectively hydrogenated to *cis*-2-butene-1,4-diol, or 2-butyne-1,4-diol could be directly hydrogenated to produce butane-1,4-diol. Using their catalysts they also found a number of other possible side reactions that could occur during the selective hydrogenation of 2-butyne-1,4-diol. They proposed that the *cis*-2-butene-1,4-diol could lose H_2O and gain H_2 to form *cis* or *trans*-crotyl alcohol, and that this *cis* or *trans*-crotyl alcohol could either go through a rearrangement to form *n*-butyraldehyde or gain a further H_2 and go onto form *n*-butanol.

When initial experiments investigating the selective hydrogenation of 2-butyne-1,4-diol were conducted at Glasgow University a similar range of reaction products were observed. From the spread of reaction products observed a reaction scheme can be proposed, detailed in Figure 6.2.2.

Figure 6.2.2 Proposed reaction scheme for this study



There are a number of differences between the reaction scheme proposed by Winterbottom et al (Figure 6.2.1) and the reaction scheme proposed in Figure 6.2.2. No *n*-butyraldehyde has been observed in any of the reactions conducted during this study. Winterbottom *et al* did not report the formation of iso-propoxytetrahydrofuran or 3-buten-1-ol [1], indeed there has been no reported literature studies that have detailed the formation of iso-proproxytetrahydro furan (and/or its "sister" products hydroxy-tetrahydrofuran and 1-(2-propanyloxy)-butan-1-ol) and 3-buten-1-ol during the selective hydrogenation of 2-butyne-1,4-diol using a supported palladium catalyst. 3-buten-1-ol can be explained by double bond migration, but clearly additional, more complex chemistry is active in the formation of iso-propoxytetrahydrofuran (and its "sister" products). The water molecules in

this reaction scheme can be thought of as hydroxyl groups and hydrogen atoms adsorbed on the catalyst surface. We attribute the hydroxyl groups to be associated with the carbon support and the hydrogen to be associated with the metal.

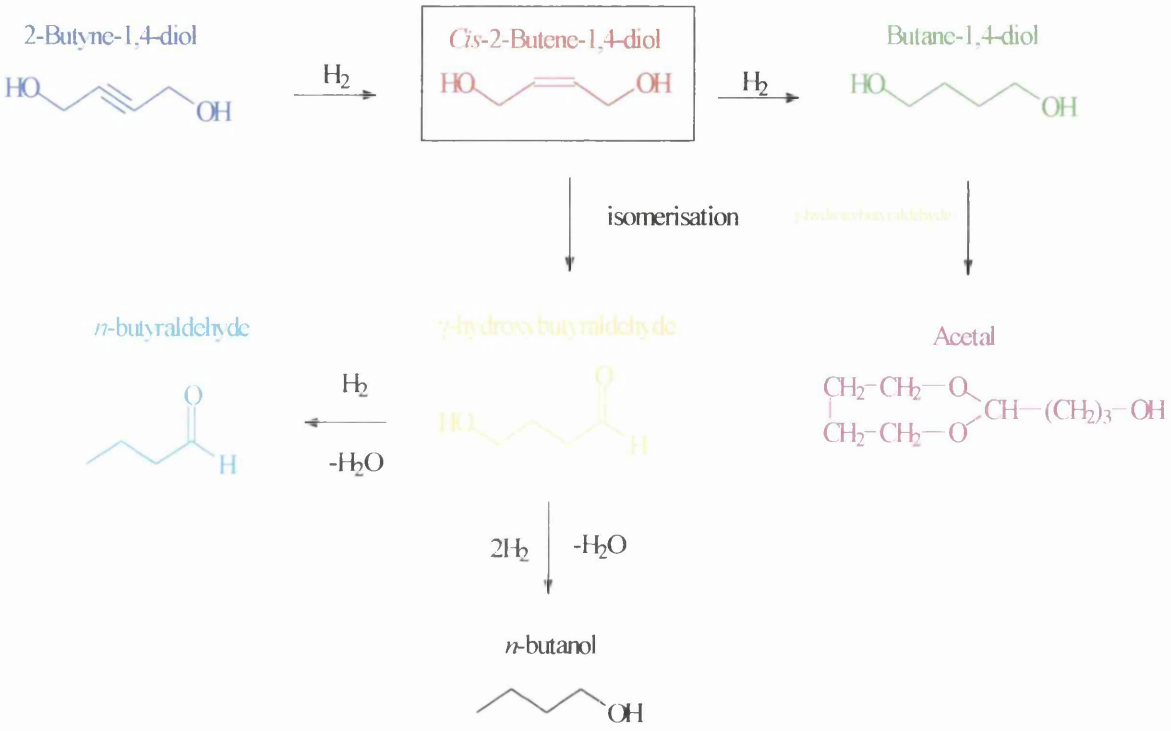
N-butyraldehyde [1, 2, 3, 4] and γ–hydroxybutyraldehyde [2, 3, 4] have been reported to have been formed during the selective hydrogenation of 2-butyne-1,4-diol by double bond migration [1, 2, 3, 4, 5] and hydrogenolysis [1, 2, 3, 4, 6, 7], these products have not been observed during any of the reactions conducted for this study, but this does not discount the possibility of double bond migration and hydrogenolysis playing an import role in the overall reaction mechanism (e.g. the formation of 3-buten-1-ol, *cis* and *trans*-crotyl alcohol and butanol).

As previously stated, iso-propoxytetrahydrofuran is an unexpected product for this type of catalytic reaction. In the literature iso-propoxytetrahydrofuran has been reported to have been produced through the reaction of 3-buten-1-ol with propan-2-ol [8], although under oxidising rather that reducing reaction conditions that are very different to those present in the ambient and elevated pressure reaction vessels employed in this study. Tedeschi found that the use of either small amounts of either phosphoric or *p*-toluenesulfonic acid in the hydrogenation of saturated diols resulted in the formation of the corresponding tetrahydrofuran and hydrocarbon [6].

While none of the literature that details the selective hydrogenation of 2-butyne-1,4-diol reports the formation of iso-propoxytetrahydrofuran, there are a couple that report the formation of an acetal (butane-1,4-diol acetal of 4-hydroxybutanal), using a supported ruthenium catalyst [3] and a supported palladium catalyst [2]. It was originally thought that iso-propoxytetrahydrofuran could have been butane-1,4-diol acetal of 4-hydroxybutanal, with the two studies that reported the formation of the acetal not employing any catalytic poisons to enhance selectivity. Chaudhari *et al* proposed the reaction scheme detailed in Figure 6.2.3 when a supported

palladium catalyst was used [2], with the reaction scheme being very similar to that proposed by Del Rosso *et al* for a study that investigated the selective hydrogenation of 2-butyne-1,4-diol employing a supported ruthenium catalyst [3]. The butane-1,4-diol acetal of 4-hydroxybutanal was formed through the reaction of γ–hydroxybutyraldehyde with butane-1,4-diol.

Figure 6.2.3 Proposed reaction scheme for the formation of butane-1,4-diol acetal of 4-hydroxybutanal



GC-MS and ^{1}H NMR confirmed that there was no production of the acetal, γ-hydroxybutyraldehyde or *n*-butyraldehyde in the reaction conducted for this project. NMR and GC-MS showed the orginally unknown molecule to be iso-proproxytetrahydrofuran (detailed in Section 5.11). The reported formation of the acetal [2, 3] helps illustrate some of the possible reaction pathways available when an unpoisoned supported catalyst is employed for the selective hydrogenation of 2-butyne-1,4-diol.

6.3 ELEVATED PRESSURE MECHANISM REACTIONS

All the experiments conducted for the development of the reaction mechanism were carried out using the elevated pressure reactor. The elevated pressure reactor was chosen over the ambient pressure reaction vessel for a number of reasons. The rate of hydrogenation is much quicker for a reaction conducted in the elevated pressure reactor when compared to the rate observed in the ambient pressure reactor (*i.e.* less reaction run time required). The sample volumes required for the GC, GC-MS, ^{1}H NMR and ^{2}D NMR analysis can be extracted from the elevated pressure reactor without having much of a detrimental effect on the overall reaction volume. As D_2 gas is quite expensive, a fully closed system (*i.e.* no continuous sparging of gas through the reaction vessel to the scavenger) allows for more efficient use of the D_2 gas.

The experiments carried out in the elevated pressure reactor were conducted at 2 bar gauge, at 65°C, employing 400ml of a 0.233M solution of 2-butyne-1,4-diol in propan-2-ol (the same as the conditions as detailed in Section 3.6). The sample volumes that were taken from the reaction vessel during the course of the reaction were around 7ml, this was to allow for enough sample to carry out GC, GC-MS analysis, ^{1}H NMR and ^{2}D NMR analysis. The activation of the catalysts was conducted *in-situ* (solvent reduction), employing 300ml of the 400ml of the propan-2-ol to activate the catalyst, with H_2 gas or D_2 gas bubbled through the stirred solvent solution, depending on the experiment. The overall mass balance and selectivities for the reactions detailed in this chapter are the same as the previously detailed elevated pressure experiment in Section 5.2.

The elevated pressure mechanism series of experiments have been designed to interrogate the reaction scheme, when they are considered in conjunction with the GC-MS data it is possible to postulate an overall reaction mechanism (detailed later). The elevated pressure mechanism experiments can be broken down into four main types. The first, is a reaction that has employed only H_2

gas to hydrogenate throughout the reaction (H_2 elevated pressure mechanism reaction, detailed in Figure 6.3.1). The second, is a reaction that has employed only D_2 gas to hydrogenate throughout the reaction (D_2 elevated pressure mechanism reaction, detailed in Figure 6.3.2). The third, is a reaction that initially employed H_2 gas to hydrogenate up to *circa* 70% conversion of the 2-butyne-1,4-diol, and then employed D_2 gas to complete the reaction (H_2/D_2 elevated pressure mechanism reaction, detailed in Figure 6.3.3). The fourth, is a reaction that initially employed D_2 gas to hydrogenate up to *circa* 70% conversion of the 2-butyne-1,4-diol, and then employed H_2 gas to complete the reaction (D_2/H_2 elevated pressure mechanism reaction, detailed in Figure 6.3.4). In Tables 6.3.3 and 6.3.4 the isotope switch is indicated by bold red type, in Figures 6.3.3 and 6.3.4 the isotope switch is indicated by arrows.

The H_2 elevated pressure reactions that were used to try and probe the reaction mechanism shows the same product distribution and selectivities that have been previously detailed here (see Figure 6.3.1 for an example). When a D_2 elevated pressure experiment was carried out that uses only D_2 gas to hydrogenate however (see Figure 6.3.2), the initial rate for the selective hydrogenation of 2-butyne-1,4-diol to *cis*-2-butene-1,4-diol was not the same as that that was originally expected. The initial rate of hydrogenation of for Figures 6.3.1 (H_2), 6.3.2 (D_2), 6.3.3 (H_2/D_2) and 6.3.4 (D_2/H_2) were 3.17×10^{-5}, 1.32×10^{-5}, 3.54×10^{-5} and 1.55×10^{-5} moles/l/s/g catalyst respectively.

There seems to be a kinetic isotope effect evident in the D_2 elevated pressure reactions. The rate of hydrogenation that is observed for the D_2 elevated pressure reaction is less than half of that observed in the H_2 elevated pressure reaction due to the use of D_2 gas to hydrogenate throughout the reaction. There also seems to be a kinetic isotope effect evident the D_2/H_2 elevated pressure reaction (Figure 6.3.4), the rate of hydrogenation when the H_2 was switched in, increased to around the rate of hydrogenation that would be observed when H_2 gas only to selectively hydrogenate the 2-butyne-1,4-diol. The kinetic isotope effect is not as pronounced in the H_2/D_2 elevated pressure reaction (Figure 6.3.3), with D_2 gas only being used to complete the reaction, the rate does not seem to significantly tail-off at the end of the reaction. This

indicated that the rate-determining step is the hydrogen-dissociation (ties in with order of reaction study) or in the cases when deuterium is initially used, deuterium-dissociation. This is possible because we do not see the kinetic isotope effect to the same extent in the H_2/D_2 elevated pressure reactions.

It only requires the loss of an OH group and the addition of one H or D atom to form 3-buten-1-ol, *cis* and *trans*-crotyl alcohol or the precursor to iso-propoxytetrahydrofuran, where the initial formation of *cis*-2-butene-1,4-diol requires the addition of two H or two D atoms. The main component to the reduced rate for the D_2 elevated pressure reactions, and the slower initial rate for the D_2/H_2 elevated pressure reactions would seem to be the rate at which D_2 dissociates to form D atoms on the catalyst surface.

There were initial problems to overcome with the ^1H NMR technique. Complex reaction solutions are not normally submitted for ^1H NMR analysis (in the low concentration ranges examined here). Ordinarily there is some purification of the sample, or at least some attempt to reduce the volume of solvent present in the sample, before NMR analysis is attempted. Ideally a sample with as few components as possible, that has had its reaction solvent removed, and the residue that is left after the solvent has been removed is diluted in a suitable solvent for NMR analysis (e.g. $CDCl_3$), is submitted for NMR analysis.

Unlike the previous NMR study that was conducted to confirm the presence of iso-propoxytetrahydrofuran (Section 5.11), no purification of the samples (after the catalyst had been filtered off) was conducted. This has the benefit that the samples have a relatively quick turn-around as little sample preparation is required before they can be analysed by ^1H NMR (preparation detailed earlier), and the reaction samples are suitable to be run neat for ^2D NMR analyses. The other major benefit is that you are dealing with a sample matrix that is the same as the sample taken form the filtered reaction solution for the ^2D NMR, and a sample matrix that has only been diluted in $CDCl_3$ for the ^1H NMR, the relationship between the relative concentrations of the 2-

butyne-1,4-diol (were applicable) and the reaction products have to each other remains unchanged.

The benefits of maintaining relative concentrations of the reaction products have to each other are manifold. It helps greatly with the assignments of both the ^{1}H NMR and ^{2}D NMR as the quantitative information from the reaction profile details the NMR peaks that should be expected. The reaction profiles can be directly related to the NMR spectra obtained without having to worry about the distortion in the relative concentrations of the products in the spectra obtained due to excessive sample pre-treatment. There are however a number of drawbacks to utilising a sample that has only been diluted in $CDCl_3$. Initially it was hoped that ^{13}C NMR spectroscopy could also be carried out on the elevated pressure reaction mechanism samples. ^{13}C NMR was tried, but it failed to produce any useful results. This was due to the dilute nature of the reaction solution even before the further dilution in $CDCl_3$. This lead to COSY spectra that only had the peaks for propan-2-ol easily observable (and a very noisy ^{13}C spectrum). This is understandable, as the maximum concentration of 2-butyne-1,4-diol in the reaction solution is 2% in propan-2-ol, before it is diluted further (1 part filtered reaction solution:4 parts $CDCl_3$) in $CDCl_3$ for the ^{1}H NMR analysis. The dilute nature of the sample solution also made it difficult to observe any peaks relating to *cis* or *trans*-crotyl alcohol, with only a few ^{1}H NMR (and fewer ^{2}D NMR) spectra detailing clearly distinguishable peaks for these species. Added with the fact that there is a certain degree of overlap of the peaks with each other in both the ^{1}H NMR and the ^{2}D NMR, assignment and interpretation of the spectra for the relatively complex reaction solutions has not been a trivial matter.

Table 6.3.1 H_2 elevated pressure reaction employing the 1% Pd/C catalyst

Time (minutes)	Butyne-1,4-diol (moles/l)	Butene-1,4-diol (moles/l)	Butane-1,4-diol (moles/l)	Butanol (moles/l)	*Cis*-crotyl alcohol (moles/l)	*T*-crotyl alcohol (moles/l)	3-butene-1-ol (moles/l)	Iso-propoxythf (moles/l)	1-(2-propanyox) (moles/l)	Conversion (%)	Selectivity (%)
0	0.2387	0	0	0	0	0	0	0	0	0	0
15	0.2069	0.0282	0	0	0	0.0019	0.0048	0.0004	0.0001	13.33	88.65
45	0.1344	0.0797	0.0039	0	0.0034	0.0058	0.0062	0.0026	0.0001	43.68	76.44
60	0.1107	0.1102	0.0048	0	0.0034	0.0058	0.0063	0.0027	0.0001	53.64	86.09
75	0.0645	0.1555	0.0080	0.0027	0.0065	0.0086	0.0114	0.0033	0.0002	72.98	89.26
90	0.0214	0.1864	0.0112	0.0035	0.0067	0.0080	0.0110	0.0003	0.0002	91.04	85.79
120	0.0086	0.1223	0.0208	0.0096	0.0114	0.0084	0.0124	0.0023	0.0011	96.42	53.12
135	0.0086	0.1024	0.0271	0.0169	0.0125	0.0065	0.0109	0.0304	0.0039	96.42	44.50
150	0.0081	0.0714	0.0327	0.0217	0.0133	0.0068	0.0117	0.0343	0.0047	96.59	30.96
210	0.0073	0.0021	0.0351	0.0236	0.0146	0.0080	0.0122	0.0439	0.0049	96.93	0.93
240	0.0073	0.0016	0.0351	0.0244	0.0141	0.0078	0.0120	0.0440	0.0047	96.94	0.71
270	0.0073	0.0014	0.0351	0.0236	0.0140	0.0079	0.0119	0.0438	0.0046	96.94	0.61
300	0.0072	0.0014	0.0352	0.0236	0.0140	0.0084	0.0119	0.0438	0.0048	96.97	0.60
330	0.0072	0.0013	0.0353	0.0236	0.0139	0.0080	0.0118	0.0438	0.0047	96.97	0.58
420	0.0072	0.0012	0.0353	0.0236	0.0142	0.0078	0.0119	0.0440	0.0048	96.97	0.51

Figure 6.3.1 Reaction profile for a H_2 elevated pressure reaction profile employing the 1% Pd/C catalyst

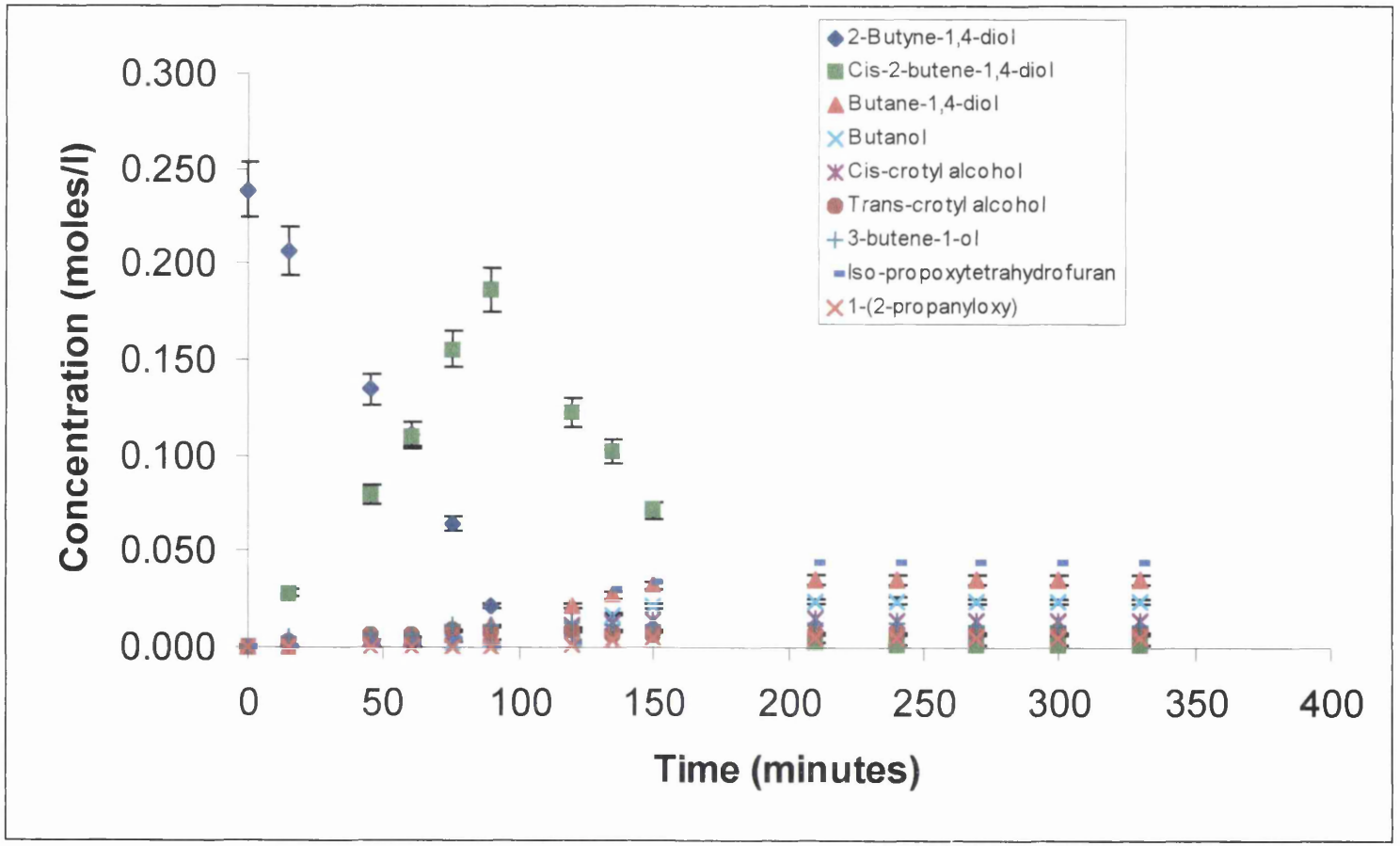


Table 6.3.2 D_2 elevated pressure reaction employing the 1% Pd/C catalyst

Time (minutes)	Butyne-1,4-diol (moles/l)	Butene-1,4-diol (moles/l)	Butane-1,4-diol (moles/l)	Butanol (moles/l)	*Cis*-crotyl alcohol (moles/l)	*T*-crotyl alcohol (moles/l)	3-butene-1-ol (moles/l)	Iso-propoxythf (moles/l)	1-(2-propanyox) (moles/l)	Conversion (%)	Selectivity (%)
0	0.2215	0	0	0	0	0	0	0	0	0	0
15	0.2134	0.0074	0	0	0	0.0019	0	0	0	3.68	90.50
30	0.2066	0.0148	0.0042	0	0	0.0022	0	0.0002	0	6.72	99.69
45	0.1938	0.0245	0.0046	0	0	0.0023	0.0039	0.0004	0	12.54	88.26
60	0.1812	0.0401	0.0047	0	0.0026	0.0029	0.0042	0.0008	0	18.20	99.55
90	0.1713	0.0448	0.0046	0	0.0026	0.0036	0.0042	0.0009	0	22.68	89.24
110	0.1460	0.0599	0.0046	0	0.0026	0.0031	0.0043	0.0012	0	34.11	79.32
120	0.1297	0.0815	0.0053	0.0002	0.0027	0.0037	0.0046	0.0019	0	41.45	88.77
150	0.0832	0.1031	0.0051	0.0003	0.0027	0.0031	0.0067	0.0022	0	62.46	74.50
165	0.0646	0.1175	0.0051	0.0007	0.0030	0.0037	0.0074	0.0024	0.0001	70.86	74.87
180	0.0534	0.1400	0.0047	0.0010	0.0032	0.0037	0.0072	0.0042	0.0001	75.88	83.26
210	0.0183	0.1445	0.0053	0.0018	0.0038	0.0078	0.0073	0.0061	0.0001	91.72	71.14
240	0.0088	0.1707	0.0057	0.0005	0.0030	0.0037	0.0074	0.0059	0.0003	96.01	80.26

Figure 6.3.2 Reaction profile for a D_2 elevated pressure reaction profile employing the 1% Pd/C catalyst

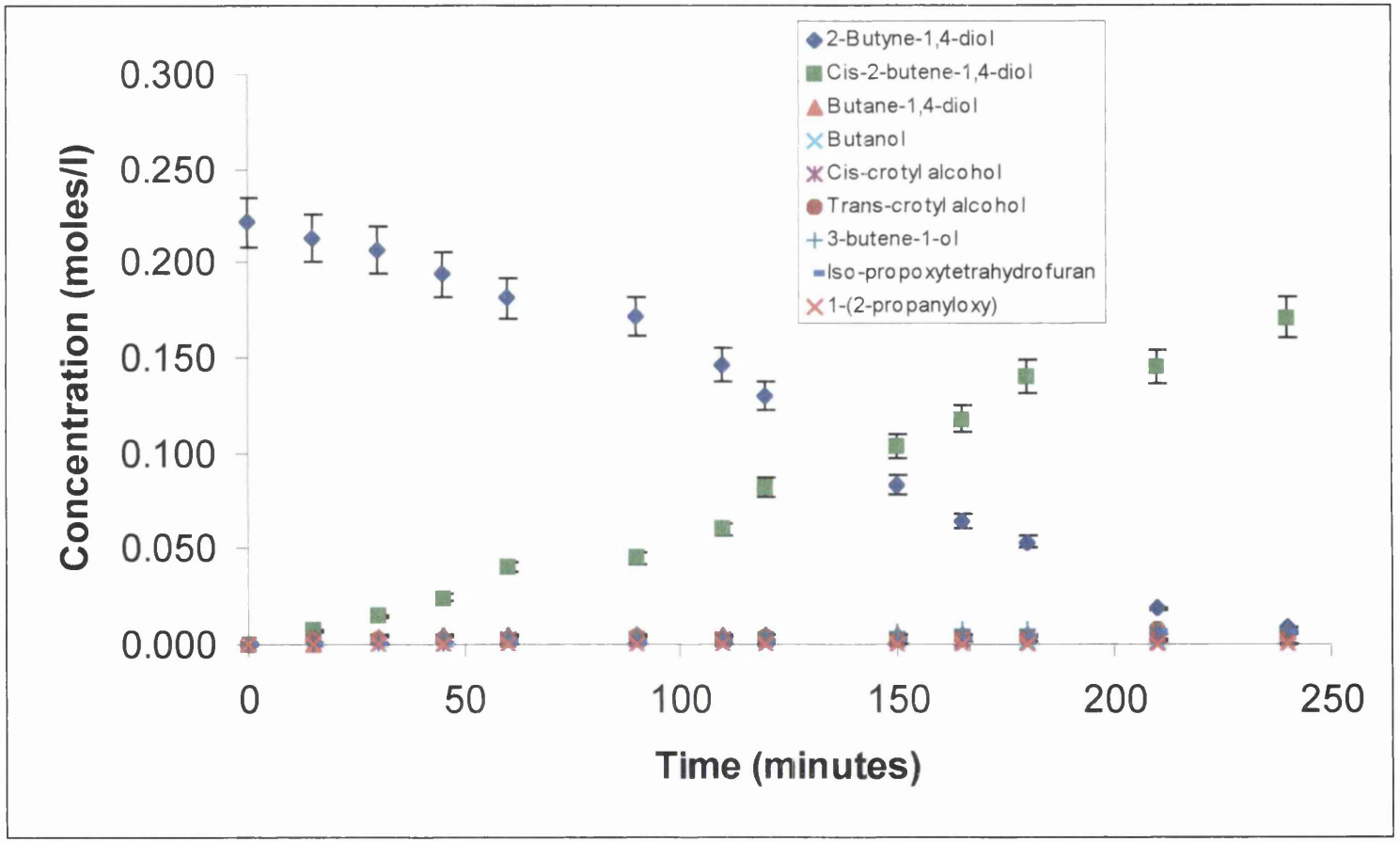


Table 6.3.3 H_2/D_2 elevated pressure reaction employing the 1% Pd/C catalyst

Time (minutes)	Butyne-1,4-diol (moles/l)	Butene-1,4-diol (moles/l)	Butane-1,4-diol (moles/l)	Butanol (moles/l)	*Cis*-crotyl alcohol (moles/l)	*T*-crotyl alcohol (moles/l)	3-butene-1-ol (moles/l)	Iso-propoxythf (moles/l)	1-(2-propanyox) (moles/l)	Conversion (%)	Selectivity (%)
0	0.2336	0	0	0	0	0	0	0	0	0	0
30	0.1626	0.0621	0	0.0002	0.0022	0.0091	0.0046	0.0001	0.0001	30.39	87.44
60	**0.0748**	**0.1490**	**0.0070**	**0.0010**	**0.0032**	**0.0181**	**0.0070**	**0.0034**	**0.0001**	**67.98**	**93.83**
70	0.0275	0.1836	0.0101	0.0032	0.0047	0.0231	0.0099	0.0083	0.0001	88.21	89.13
90	0.0093	0.1211	0.0224	0.0092	0.0080	0.0212	0.0118	0.0220	0.0001	96.00	54.00
120	0.0080	0.0415	0.0350	0.0212	0.0095	0.0116	0.0121	0.0382	0.0001	96.57	18.38
150	0.0087	0.0149	0.0435	0.0295	0.0073	0.0071	0.0113	0.0416	0.0001	96.28	6.61
180	0.0078	0.0054	0.0438	0.0326	0.0095	0.0049	0.0131	0.0435	0.0001	96.65	2.39
210	0.0079	0.0023	0.0428	0.0336	0.0123	0.0041	0.0121	0.0438	0.0014	96.62	1.01
240	0.0079	0.0029	0.0415	0.0331	0.0124	0.0077	0.0121	0.0436	0.0048	96.62	1.31
270	0.0078	0.0025	0.0412	0.0331	0.0116	0.0076	0.0124	0.0426	0.0049	96.67	1.111
300	0.0075	0.0025	0.0416	0.0321	0.0136	0.0077	0.0121	0.0435	0.0049	96.79	1.10
360	0.0074	0.0016	0.0412	0.0318	0.0139	0.0078	0.0123	0.0427	0.0047	96.82	0.73
420	0.0072	0.0016	0.0405	0.0314	0.0136	0.0076	0.0123	0.0429	0.0048	96.92	0.69

Figure 6.3.3 Reaction profile for a H_2/D_2 elevated pressure reaction profile employing the 1% Pd/C catalyst

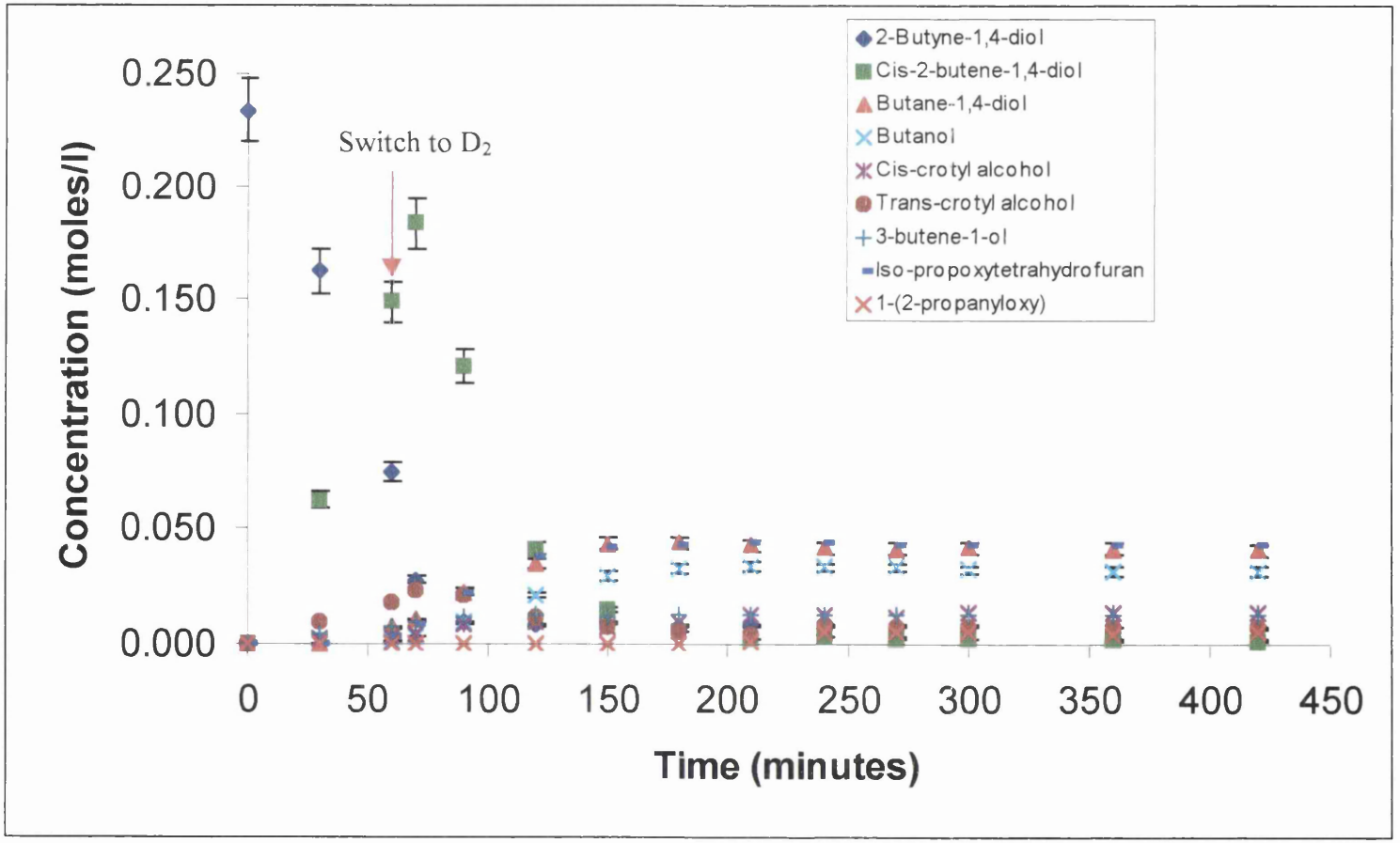
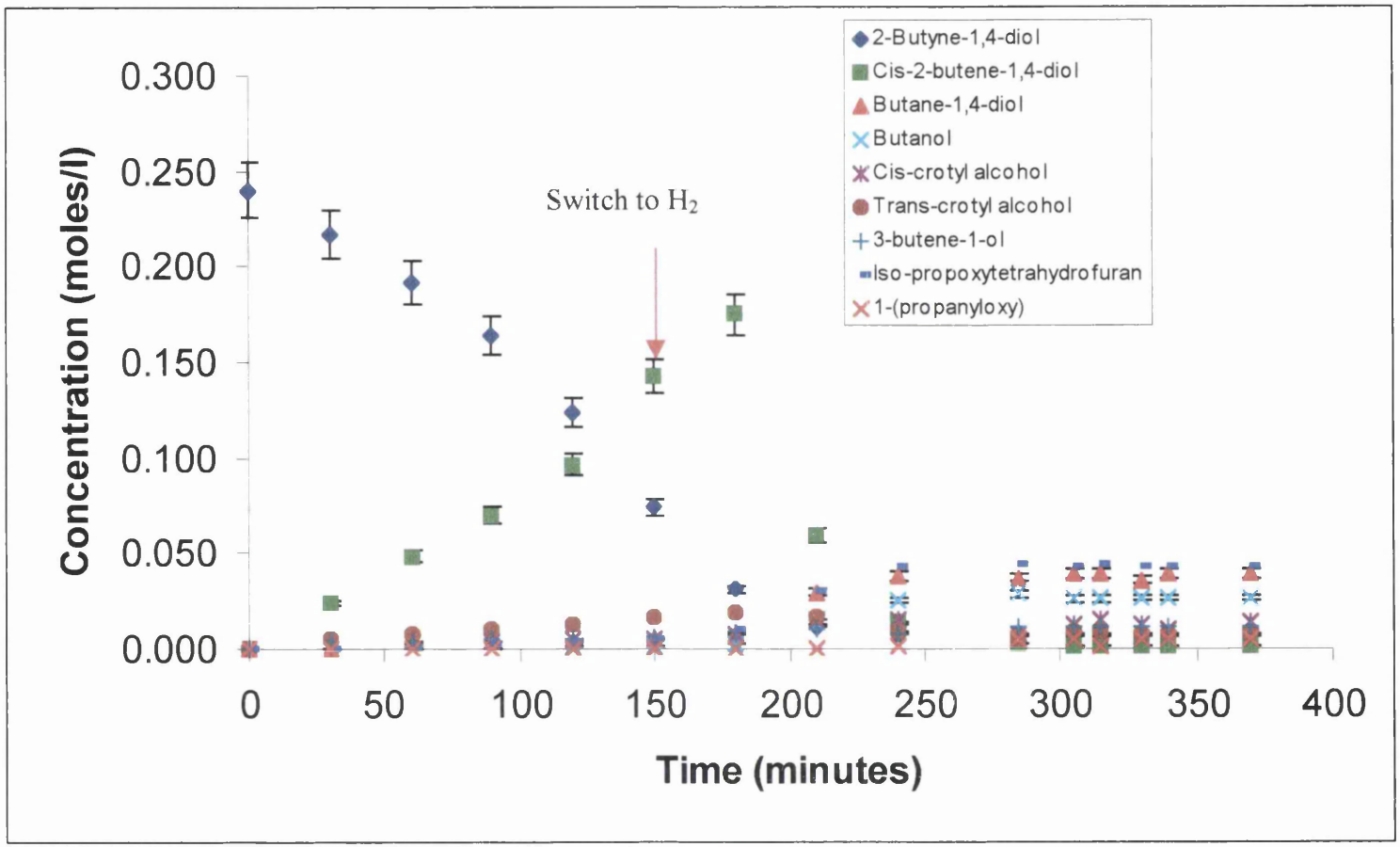


Table 6.3.4 D_2/H_2 elevated pressure reaction employing the 1% Pd/C catalyst

Time (minutes)	Butyne-1,4-diol (moles/l)	Butene-1,4-diol (moles/l)	Butane-1,4-diol (moles/l)	Butanol (moles/l)	*Cis*-crotyl alcohol (moles/l)	*T*-crotyl alcohol (moles/l)	3-butene-1-ol (moles/l)	Iso-propoxythf (moles/l)	1-(2-propanyox) (moles/l)	Conversion (%)	Selectivity (%)
0	0.2400	0	0	0	0	0	0	0	0	0	0
30	0.2168	0.0242	0	0	0	0.0050	0.0038	0.0004	0.0001	9.67	104.23
60	0.1915	0.0483	0.0032	0.0002	0.0040	0.0074	0.0043	0.0010	0.0001	20.21	99.67
90	0.1638	0.0696	0.0035	0.0005	0.0043	0.0097	0.0048	0.0020	0.0001	31.76	91.27
120	0.1238	0.0964	0.0042	0.0008	0.0048	0.0127	0.0055	0.0033	0.0001	48.41	82.93
150	**0.0742**	**0.1425**	**0.0052**	**0.0014**	**0.0055**	**0.0160**	**0.0066**	**0.0055**	**0.0001**	**69.10**	**85.94**
180	0.0310	0.1750	0.0074	0.0027	0.0071	0.0194	0.0087	0.0099	0.0001	87.07	83.74
210	0.0117	0.0589	0.0292	0.0140	0.0148	0.0168	0.0106	0.0300	0.0001	95.14	25.79
240	0.0078	0.0133	0.0377	0.0249	0.0148	0.0093	0.0075	0.0428	0.0014	96.73	5.75
285	0.0073	0.0021	0.0371	0.0284	0.0081	0.0047	0.0112	0.0438	0.0049	96.95	0.91
305	0.0072	0.0016	0.0394	0.0258	0.0126	0.0088	0.0116	0.0433	0.0049	97.00	0.70
315	0.0072	0.0013	0.0393	0.0261	0.0148	0.0083	0.0116	0.0435	0.0015	97.00	0.58
330	0.0072	0.0012	0.0356	0.0264	0.0129	0.0079	0.0116	0.0430	0.0047	97.01	0.52
340	0.0071	0.0012	0.0390	0.0264	0.0103	0.0078	0.0116	0.0431	0.0047	97.03	0.51
370	0.0071	0.0011	0.0388	0.0262	0.0134	0.0072	0.0116	0.0432	0.0048	97.04	0.49

Figure 6.3.4 Reaction profile for a D_2/H_2 elevated pressure reaction profile employing the 1% Pd/C catalyst



6.4 NMR ASSIGNMENTS FOR REACTION REAGENTS IN PROPAN-2-OL

In conjunction with Dr. David Rycroft a series of trial NMR spectra were produced to try and find a suitable protocol for sample preparation. The conclusion from the trial spectra was that the sample solution from the reaction vessel could be diluted in $CDCl_3$ without the need for purification and pre-concentration for the ^1H NMR spectra, and that the sample solution could be analysed neat for the ^2D NMR spectra. The sample preparation had the benefit of producing a solution that was easily comparable with the parent, filtered reaction solution. Indeed, more confidence in the NMR results can be derived from the fact that the relative distributions of the reaction products have not been compromised, despite the complex nature of the spectra, the NMR assignments are detailed in Table 6.4.1 below. Standards were run in propan-2-ol at the concentration range employed by the reactions for each of the products. The standards were compared with the Aldrich ^1H NMR spectra.

Table 6.4.1

	Ref	Proton	Chemical Shift	Signal
a) 2-butyne-1,4-diol	9a	1a	4.23	Singlet
b) *cis*-2-butene-1,4-diol	9b	1b	4.15	Doublet
		2b	5.75	triplet
c) Butane-1,4-diol	9c	1c	3.61	triplet
		2c	1.66	t of d
d) Butanol	9d	1d	3.61	triplet
		2d	1.54	t of t
		3d	1.38	t of d
		4d	0.90	triplet
e) Crotyl alcohol	9d	1e	4.05	doublet
		2e	5.65	d of t
		3e	5.65	d of q
		4e	1.70	doublet
f) 3-buten-1-ol	9e	1f	3.65	triplet
		2f	2.33	d of t
		3f	5.82	t of t
		4f	5.09	doublet
g) Iso-proproxythf		3g	1.85	d of t
		4g	2.00	t of t
		5g	3.75	triplet
		7g	1.05	doublet
		8g	5.22	triplet

It was not possible to discriminate between *cis* and *trans*-crotyl alcohol in the NMR samples were run during the course of this study, due to the relatively low concentrations of *cis* and *trans*-crotyl alcohol produced during the course of the reaction.

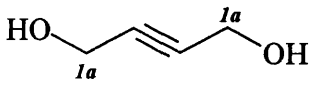
The chemical shifts and assignments detailed in the assignment table where obtained by diluting down a 2% solution of the reagent in propan-2-ol to give sample matrix that was as close as possible to that produced during reaction. This 2% standard solution was then diluted further with $CDCl_3$ (1 part standard solution:4 parts $CDCl_3$) to allow the ^1H NMR to be run at room temperature. All the experimental results for the for the elevated pressure mechanism reactions employing ^1H NMR spectra, were run by taking the reaction solution, filtering-off the catalyst, and diluting 1ml of the reaction solution with 4ml of $CDCl_3$. Unlike the previous study to confirm the iso-propoxytetrahydrofuran, no pre-concentration or purification of the samples was utilised for any of the elevated pressure mechanism reactions.

The ^2D NMR spectra were run neat, with the sample vessel requiring around 5ml of filtered reaction solution. The assignments for the ^2D NMR spectra obtained from the elevated pressure mechanism reactions are based on the assignments for the ^1H NMR, with corrections made by using the chemical shift of the secondary methyl groups on propan-2-ol (1.188ppm), with the original as recorded spectra displayed here. The chemical shift for the secondary methyl groups was obtained by examining the ^1H NMR spectrum of one of the standard solutions. The corrections were made to the ^2D spectra by subtracting or adding the difference in ppm between the chemical shifts of the propan-2-ol methyl groups in the ^1H NMR and the propan-2-ol methyl groups in the ^2D NMR as required, because of drift experienced with the ^2D NMR spectrometer.

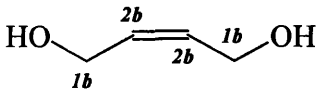
Figure 6.4.1 is a graphical summary of the NMR assignments for the analyses of interest.

Figure 6.4.1 NMR assignment graphical summary

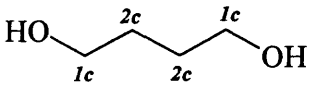
a) 2-Butyne-1,4-diol



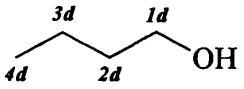
b) *Cis*-2-Butene-1,4-diol



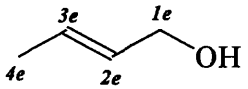
c) Butane-1,4-diol



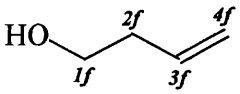
d) *N*-butanol



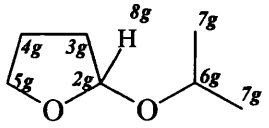
e) *Cis* or *Trans*-Crotyl Alcohol



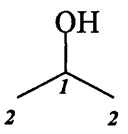
f) 3-Buten-1-ol



g) Iso-propoxytetrahydrofuran



Propan-2-ol



6.5 SUMMARY OF NMR OBTAINED FROM THE ELEVATED PRESSURE MECHANISM REACTIONS

The ^{1}H and ^{2}D NMR spectra that are considered here are representative spectra for the different elevated pressure mechanism experiments. The spectra represent three main time periods during the reaction profile. The first period that is represented by the spectra is in the initial stages of the reaction between 10 and 20% conversion of the 2-butyne-1,4-diol. The second period that is represented is between 60 and 70% conversion of the 2-butyne-1,4-diol, just before all the 2-butyne-1,4-diol has been hydrogenated and the onset of the majority of the production of iso-propoxytetrahydrofuran, butanol, butane-1,4-diol *cis* and *trans*-crotyl alcohol and 3-buten-ol from the hydrogenation and reaction of the *cis*-2-butene-1,4-diol. The third period that is represented is at 200%, when all the reaction has been completed. There has however, been a number of spectra taken at differing time periods for the different elevated pressure mechanism reactions such as 40% conversion of the 2-butyne-1,4-diol (same peaks observed as in the 10,20 and 60% conversion spectra), 140% and 160% conversion of the butyne-1,4-diol (both of which look very similar to the spectra for 200% conversion, with the only addition being peaks for *cis*-2-butene-1,4-diol), these have been omitted because of their similarities to the spectra detailed here.

The H_2 elevated pressure mechanism reaction (Figure 6.3.1) was carried out to act essentially as a blank experiment for the series of elevated pressure mechanism reactions. It can be thought off as a benchmark experiment, by which all the other elevated pressure mechanism reaction experiments in the series can be compared to. It was an experiment that employed only H_2 gas to hydrogenate, following the same reaction protocols as the elevated pressure experiments conducted previously. Figure 6.5.1 a) is a ^{1}H NMR spectrum that corresponds to a reaction profile at which there has been 10% conversion of the 2-butyne-1,4-diol in a H_2 elevated pressure reaction. A peak corresponding to the 1a protons in 2-butyne-1,4-diol can be observed at 4.23ppm. Peaks corresponding to the 1b and 2b protons in *cis*-2-butene-1,4-diol can be

observed at 4.15ppm and 5.73ppm respectively. These peaks agree with what has been observed in the previously run spectra for the standard solutions.

Figure 6.5.1 b) is a ^{1}H NMR spectrum that is representative of a reaction profile at 70% conversion of the 2-butyne-1,4-diol, employing only H_2 gas to hydrogenate. A peak corresponding to the 1a protons in 2-butyne-1,4-diol can be observed at 4.23ppm. Peaks corresponding to the 1b and 2b protons in *cis*-2-butene-1,4-diol can be observed at 4.15ppm and 5.73ppm respectively. At 70% conversion of the 2-butyne-1,4-diol, peaks corresponding to the 1c and 2c protons in butane-1,4-diol can be observed at 3.61ppm and 1.66ppm respectively. Peaks corresponding to the 1d, 2d, 3d and 4d protons in butanol can be observed at 3.61ppm, 1.54ppm, 1.38ppm and 0.90ppm respectively. Peaks corresponding to the 1f, 2f, 3f and 4f protons in 3-buten-1-ol can be observed at 3.65ppm, 2.33ppm, 5.82ppm and 5.09ppm respectively. Peaks corresponding to the 3g, 4g, 5g, 7g and 8g protons in iso-propoxytetrahydrofuran can be observed at 1.85ppm, 2.00ppm, 3.75ppm, 1.05ppm and 5.22ppm respectively. Although the reaction is at only 70% conversion of 2-butyne-1,4-diol (it has been stated previously that a small amount of formation of the side products can be observed before all the 2-butyne-1,4-diol has been completely hydrogenated), peaks for butane-1,4-diol, butanol, 3-buten-1-ol and iso-propoxytetrahydrofuran can be observed in the ^{1}H NMR spectrum is plotted at a high magnification.

Figure 6.5.1 c) is an example of a ^{1}H NMR spectrum that details a reaction that is at 200% conversion of 2-butyne-1,4-diol and has only used H_2 gas to hydrogenate. Peaks corresponding to the 1c and 2c protons in butane-1,4-diol can be observed at 3.61ppm and 1.66ppm respectively. Peaks corresponding to the 1d, 2d, 3d and 4d protons in butanol can be observed at 3.61ppm, 1.54ppm, 1.38ppm and 0.90ppm respectively. Peaks corresponding to the 1f, 2f, 3f and 4f protons in 3-buten-1-ol can be observed at 3.61ppm. Peaks corresponding to the 3g, 4g, 5g, 7g and 8g protons in iso-propoxytetrahydrofuran can be observed at 1.85ppm, 2.00ppm, 3.75ppm, 1.05ppm and 5.22ppm respectively.

All the ^{2}D NMR spectra that correspond to the ^{1}H NMR spectra for the H_2 elevated pressure mechanism reaction show the same peaks. The ^{2}D probe only scans for species containing deuterium, so when H_2 gas is only used to hydrogenate the reaction products are not visible to the ^{2}D probe. The ^{2}D NMR show only propan-2-ol, positions 1, 2 and the OD proton in the propan-2-ol at 3.954ppm, 1.188ppm and 4.907ppm respectively these can be seen in Figure 6.5.2 (with the D signals being due to natural abundance).

Figure 6.5.3 a) is a ^{1}H NMR spectrum for the D_2 elevated pressure reaction that details a reaction that is at 10% conversion of 2-butyne-1,4-diol. As in the H_2 elevated pressure reaction a peak corresponding to the 1a protons in 2-butyne-1,4-diol can be observed at 4.23ppm. There is also a peak corresponding to the 1b protons in *cis*-2-butene-1,4-diol that can be observed at 4.15ppm, the peak for the 1b protons has lost its multiplicity due to the fact that the positions at 2b are occupied by D atoms, this is as expected for a reaction using D_2 gas to hydrogenate. There should be no peak at 5.73ppm because D atoms occupy the 2b position. There is a very small peak however, due to residual H_2 gas in the D_2, or hydrogen/deuterium exchange via the catalyst support.

Figure 6.5.3 b) is an example of a ^{1}H NMR spectrum that is representative of a reaction at 60% conversion of 2-butyne-1,4-diol, that has used only D_2 gas to hydrogenate. A peak corresponding to the 1a protons in 2-butyne-1,4-diol can be observed at 4.23ppm. A peak corresponding to the 1b protons in *cis*-2-butene-1,4-diol can be observed at 4.15ppm, the peak for the 1b protons, as in the previous spectrum has lost its multiplicity because the positions at 2b are occupied by D atoms. There should be no peak at 5.73ppm because D atoms occupy the 2b position, this peak is only observed due to the reasons outlined earlier.

Figure 6.5.3 c) is a ^{1}H NMR spectrum in Figure 6.5.3 represents a D_2 elevated pressure reaction with a 200% conversion of 2-butyne-1,4-diol. A peak corresponding to the 1c in butane-1,4-diol can be observed at 3.61ppm. Only peaks corresponding to positions 3d and 4d can be observed for the butanol at

1.38ppm and 0.90ppm respectively. Peaks corresponding to the positions 3g, 4g in iso-propoxytetrahydrofuran are present at 1.85ppm and 2.00ppm respectively. The fact that peaks can be seen for positions 3g and 4g in the iso-propoxytetrahydrofuran is consistent with positions 3g and 4g having at least one D atom each. A peak corresponding to the 8g proton in iso-proproxytetrahydro furan can be observed at 5.22ppm. Proton 8g has lost multiplicity due to the incorporation of D atoms into the furan ring. The fact that proton can still be observed however, means that it must originate from a position of a precursor species that has an H atom present and not a D atom. A peak for the 5g position in iso-propoxytetrahydrofuran can not be observed, to confirm the presence of one or more D atoms in the 5g position the ^{2}D NMR spectra for this reaction will have to be examined.

Unlike in the case for the elevated pressure reaction mechanism reactions that employed H_2 gas to hydrogenate, when D_2 gas was used to hydrogenate other peaks apart from those that could be attributed to propan-2-ol could also be seen in the ^{2}D NMR in the spectra in Figure 6.5.4.

Figure 6.5.4 a) is a ^{2}D NMR spectrum for the D_2 elevated pressure reaction at 10% conversion of 2-butyne-1,4-diol that shows the 1, 2 and OD protons in the propan-2-ol at 3.969ppm, 1.188ppm and 4.939ppm respectively. A peak corresponding to the 2b protons in *cis*-2-butene-1,4-diol can be observed at 5.686ppm. A peak corresponding to the 2c in butane-1,4-diol can be observed at 1.601ppm. Peaks corresponding to the 2d, 3d and 4d protons in butanol can be observed at, 1.585ppm, 1.363ppm and 0.902ppm respectively. Peaks corresponding to protons 3g and 4g in iso-propoxytetrahydrofuran can be observed at 1.776ppm and 1.983ppm respectively. The presence of peaks for the 3g and 4g positions in iso-propoxytetrahydrofuran indicates that there is at least one D atom in positions 3g and 4g. The fact that products such as iso-propoxytetrahydrofuran can be observed at only 10% conversion of the 2-butyne-1,4-diol is a testament to the sensitivity of the ^{2}D probe (the peaks for propan-2-ol only apparent because of natural abundance of D atoms), it also shows that there is minor conversion of the *cis*-2-butene-1,4-diol when there is still 2-butyne-1,4-diol present in the reaction solution. Although it is not

possible to tell the multiplicity of the peaks in the ^2D NMR spectra, it is possible to observe molecules containing D atoms in them at relatively low concentrations. The G.C. is not as sensitive as the ^2D NMR technique when it comes to the detection of very low levels of "side products", although very minor amounts can be produced through the reaction of *cis*-2-butene-1,4-diol, 2-butyne-1,4-diol effectively blocks almost all of the access to the active sites for *cis*-2-butene-1,4-diol until all the 2-butyne-1,4-diol has been depleted.

Figure 6.5.4 b) is a ^2D NMR spectrum for the D_2 elevated pressure reaction at 60% conversion of 2-butyne-1,4-diol, this shows propan-2-ol, positions 1, 2 and the OD proton in the propan-2-ol at 3.969ppm, 1.188ppm and 4.939ppm respectively. A peak corresponding to the 2b protons in *cis*-2-butene-1,4-diol can be observed at 5.686ppm. A peak corresponding to the 2c in butane-1,4-diol can be observed at 1.601ppm. Peaks corresponding to the 2d, 3d and 4d protons in butanol can be observed at, 1.585ppm, 1.363ppm and 0.902ppm respectively. Peaks corresponding to protons 3g and 4g in iso-propoxytetrahydrofuran can be observed at 1.776ppm and 1.983ppm respectively, with no peak for 5g observed. We do not observe any peak for proton 8g, meaning that it is not a D atom. This spectrum correspond to 60% reaction of the 2-butyne-1,4-diol.

Figure 6.5.4 c) is a ^2D NMR spectrum for the D_2 elevated pressure reaction at 200% conversion of 2-butyne-1,4-diol, this shows propan-2-ol, 1, 2 and OD protons in the propan-2-ol at 3.954ppm, 1.188ppm and 4.854ppm respectively. A peak corresponding to the 2c in butane-1,4-diol can be observed at 1.585ppm. . Peaks corresponding to the 2d, 3d and 4d protons in butanol can be observed at, 1.585ppm, 1.363ppm and 0.902ppm respectively. Peaks corresponding to protons 3g and 4g in iso-propoxytetrahydrofuran can be observed at 1.824ppm and 1.967ppm respectively, with no peak for 5g easily discernible. Again we do not observe any peak for proton 8g in the iso-propoxytetrahydrofuran. The lack of a peaks in Figure 6.5.4 b) and 6.5.4 c) in the 5g and 8g positions of iso-propoxytetrahydrofuran means that there is no D atom in either of these positions. This has implications for the reaction mechanism.

The H_2/D_2 elevated pressure reaction was conducted with H_2 being used to hydrogenate up to circa 70% reaction, then the hydrogenation was allowed to continue to 200% using D_2. The D_2/H_2 elevated pressure reaction was conducted with D_2 being used to hydrogenate up to circa 70% reaction, then the hydrogenation was allowed to continue to 200% using H_2. The 10% and 70% spectra for the H_2/D_2 elevated pressure reaction have been omitted here because they are essentially the same as the spectra for the H_2 elevated pressure reaction. The 10% and 70% spectra for the D_2/H_2 elevated pressure reaction have also been omitted here because they are essentially the same as the spectra for the D_2 elevated pressure reaction.

Figure 6.5.5 a) is a ^1H NMR spectrum that represents 200% conversion of the 2-butyne-1,4-diol for a H_2/D_2 elevated pressure reaction, peaks corresponding to the 1c and 2c protons in butane-1,4-diol can be observed at 3.61ppm and 1.66ppm respectively. Peaks corresponding to the 1d, 2d, 3d and 4d protons in butanol can be observed at 3.61ppm, 1.54ppm, 1.38ppm and 0.90ppm respectively. Peaks corresponding to the 3g, 4g, 5g, 7g and 8g protons in iso-propoxytetrahydrofuran can be observed at 1.85ppm, 2.00ppm, 3.75ppm, 1.05ppm and 5.22ppm respectively. There appears to be no loss in multiplicity in the 8g proton unlike in other reactions that only use D_2 gas to hydrogenate.

Figure 6.5.5 b) ^1H NMR spectrum that represents 200% conversion of 2-butyne-1,4-diol for a D_2/H_2 elevated pressure reaction, peaks corresponding to the 1c and 2c protons in butane-1,4-diol can be observed at 3.61ppm and 1.66ppm respectively. Peaks corresponding to the 1d, 2d, 3d and 4d protons in butanol can be observed at 3.61ppm, 1.54ppm, 1.38ppm and 0.90ppm respectively. A Peak corresponding to the 1f protons in 3-buten-1-ol can be observed at 3.61ppm. Peaks corresponding to the 3g, 4g, 5g, 7g and 8g protons in iso-propoxytetrahydrofuran can be observed at 1.85ppm, 2.00ppm, 3.75ppm, 1.05ppm and 5.22ppm respectively. There appears to be loss in multiplicity in the 8g proton like in other reactions that only use D_2 gas to hydrogenate, but it must be noted that the resolution for this spectrum is poor, due to instrumentation problems.

Figure 6.5.6 a) is a ^{2}D NMR spectrum that represents 200% conversion of 2-butyne-1,4-diol for a H_2/D_2 elevated pressure reaction that shows propan-2-ol, positions 1, 2 and the OD proton in the propan-2-ol at 3.955ppm, 1.188ppm and 4.920ppm respectively. A peak corresponding to the 2c in butane-1,4-diol can be observed at 1.628ppm. . Peaks corresponding to the 2d, 3d and 4d protons in butanol can be observed at, 1.628ppm, 1.395ppm and 0.994ppm respectively. Peaks corresponding to protons 3g and 4g in iso-propoxytetrahydrofuran can be observed at 1.846ppm and 2.038ppm respectively. This represents 200% conversion of 2-butyne-1,4-diol in the H_2/D_2 elevated pressure mechanism reaction.

Figure 6.5.6 b) is a ^{2}D NMR spectrum that represents 200% conversion of 2-butyne-1,4-diol for a D_2/H_2 that shows propan-2-ol, 1, 2 and OD protons in the propan-2-ol at 3.955ppm, 1.188ppm and 4.920ppm respectively. A peak corresponding to the 2c in butane-1,4-diol can be observed at 1.623ppm. . Peaks corresponding to the 2d, 3d and 4d protons in butanol can be observed at, 1.623ppm, 1.395ppm and 0.942ppm respectively. Peaks corresponding to protons 3g and 4g in iso-propoxytetrahydrofuran can be observed at 1.846ppm and 1.991ppm respectively.

The H_2/D_2 and D_2/H_2 elevated pressure reactions did not produce spectra for the 200% conversion of 2-butyne-1,4-diol samples that were initially anticipated. For the 200% conversion of 2-butyne-1,4-diol, the ^{1}H NMR and ^{2}D NMR spectra for both the H_2/D_2 elevated pressure reaction and D_2/H_2 elevated pressure reaction are not clearly distinguishable from each other.

Figure 6.5.1 ^1H spectra for H_2 elevated pressure reaction

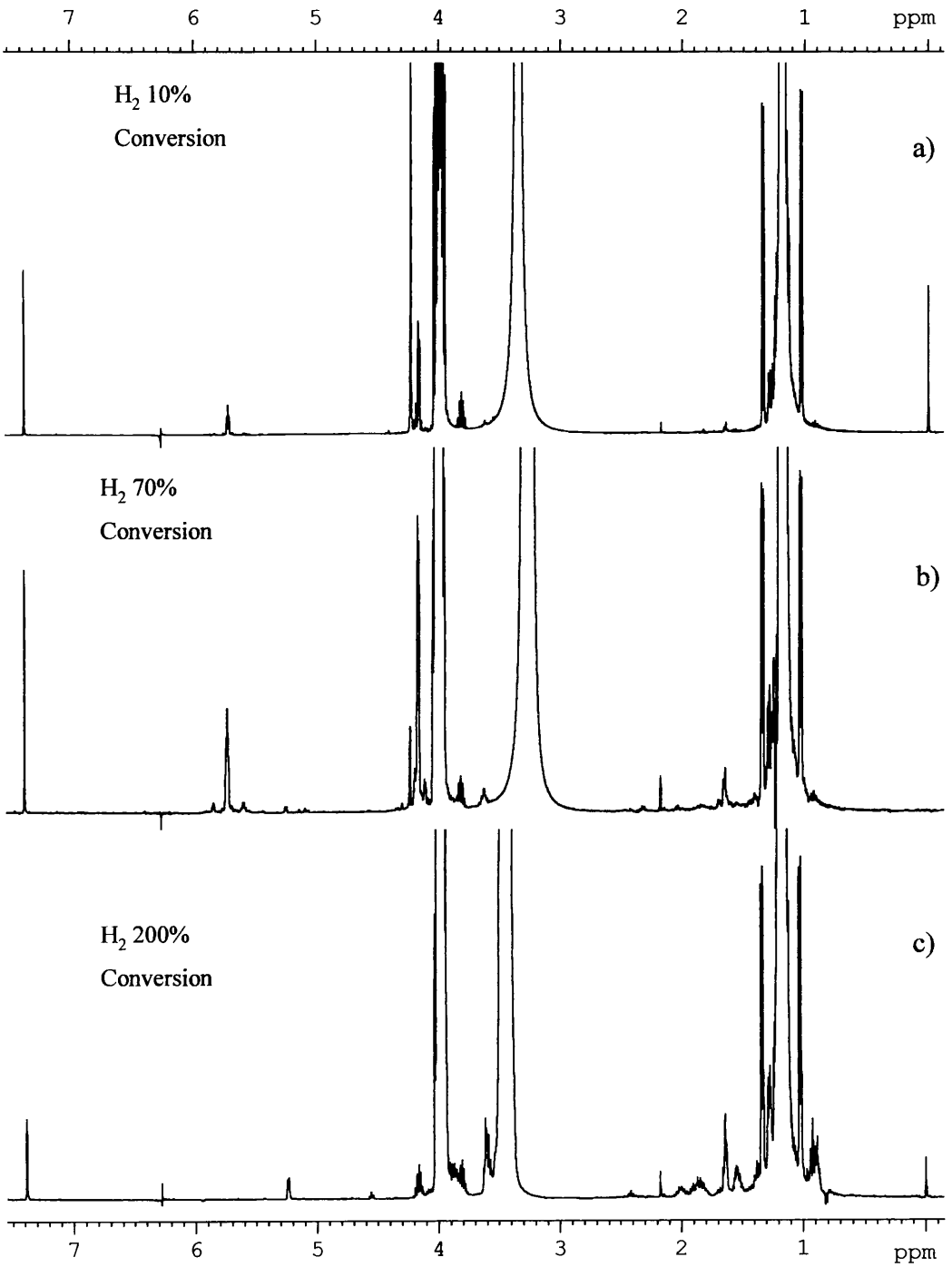


Figure 6.5.2 ^{2}D spectra for H_2 elevated pressure reaction

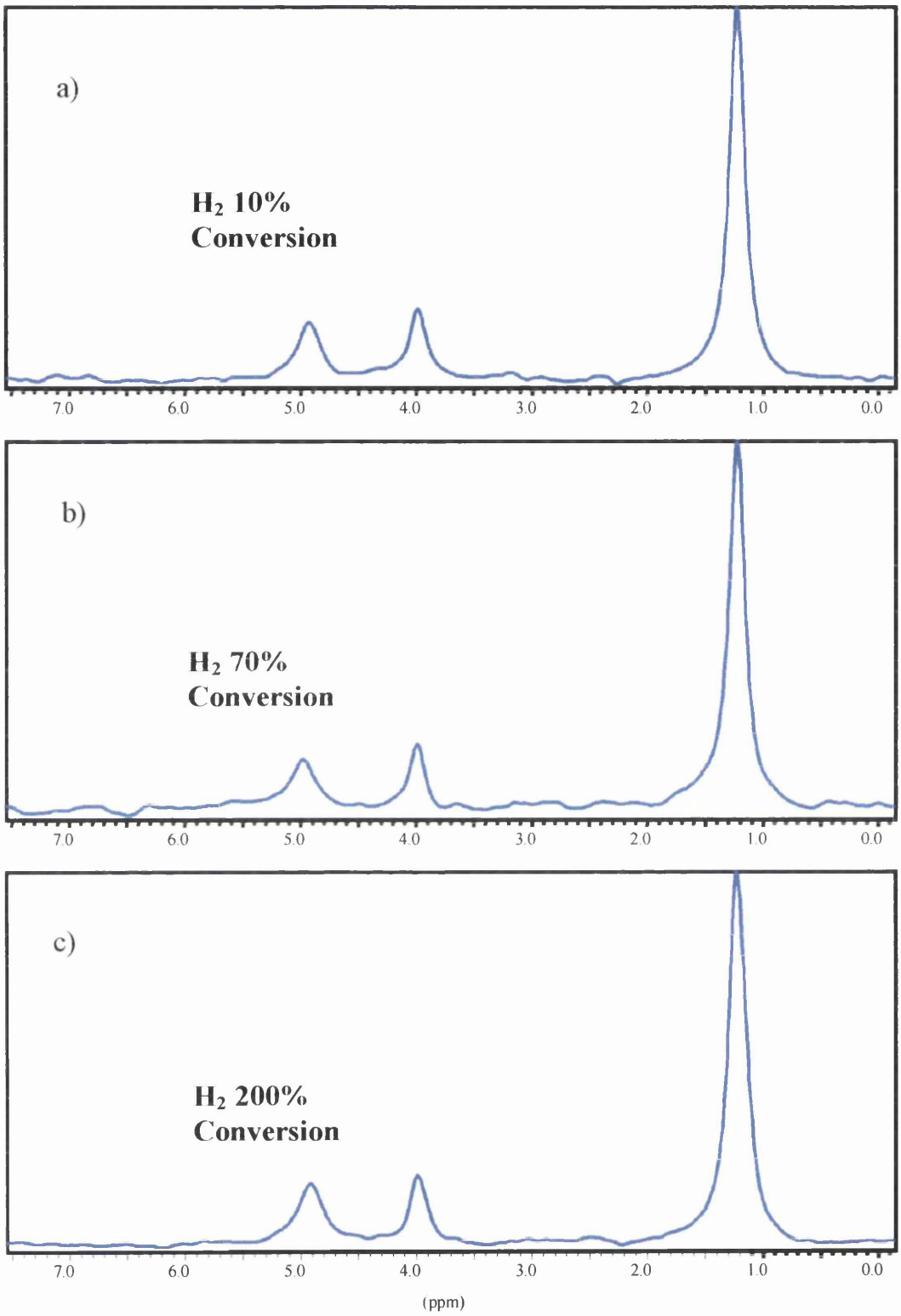


Figure 6.5.3 ^1H spectra for D_2 elevated pressure reaction

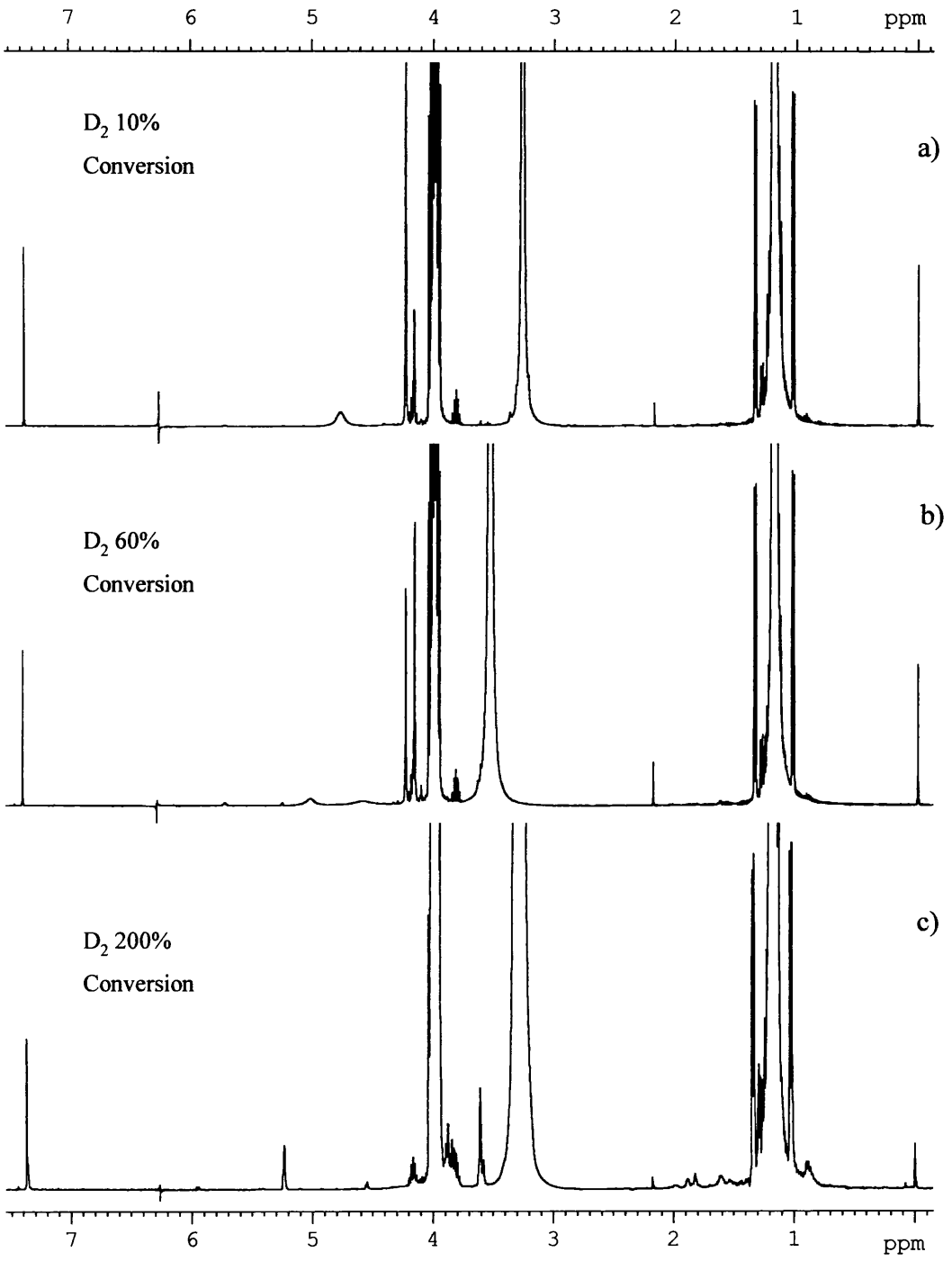


Figure 6.5.4 ^{2}D spectra for D_2 elevated pressure reaction

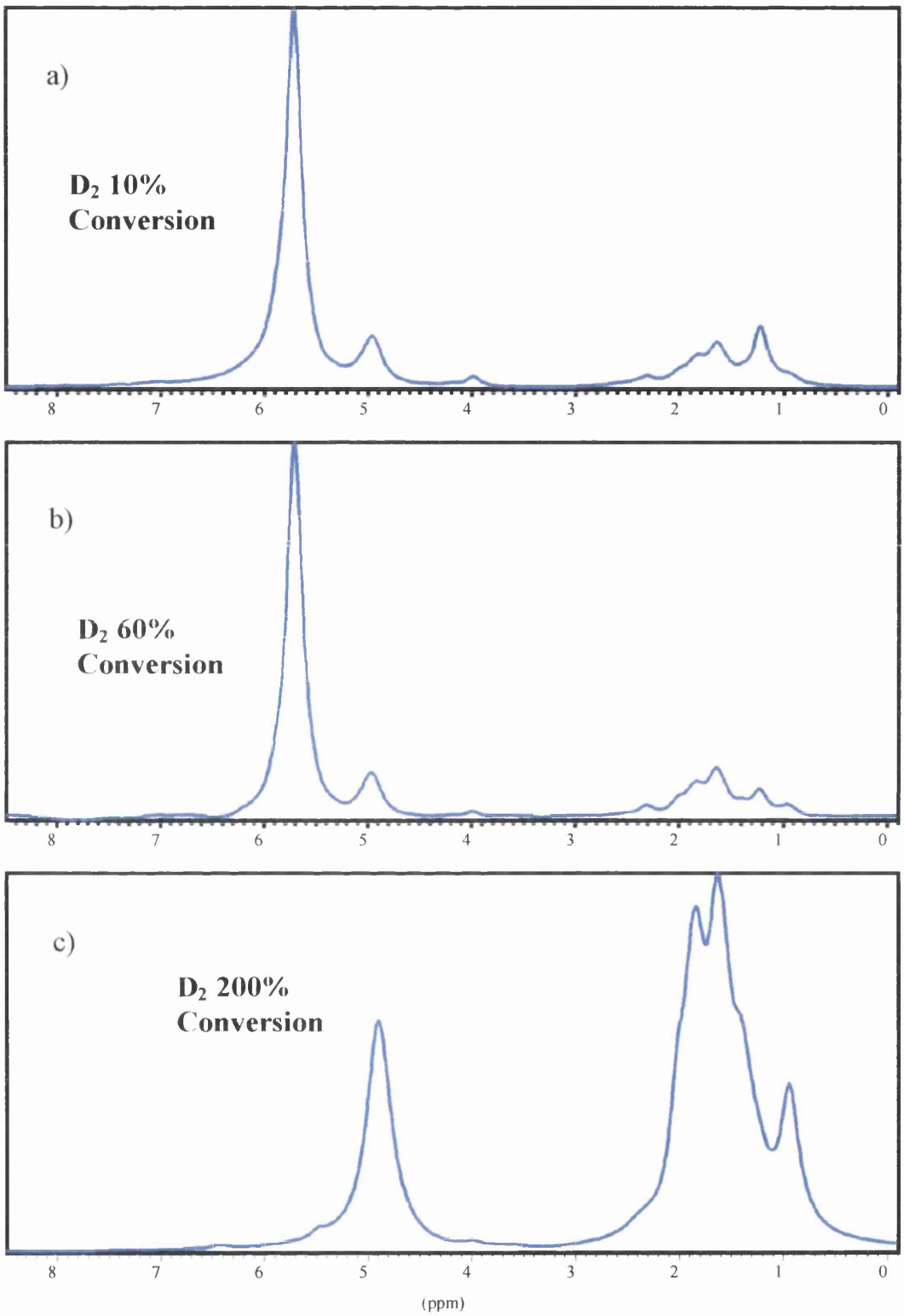


Figure 6.5.5 ^1H spectra for H_2/D_2 and D_2/H_2 elevated pressure reactions

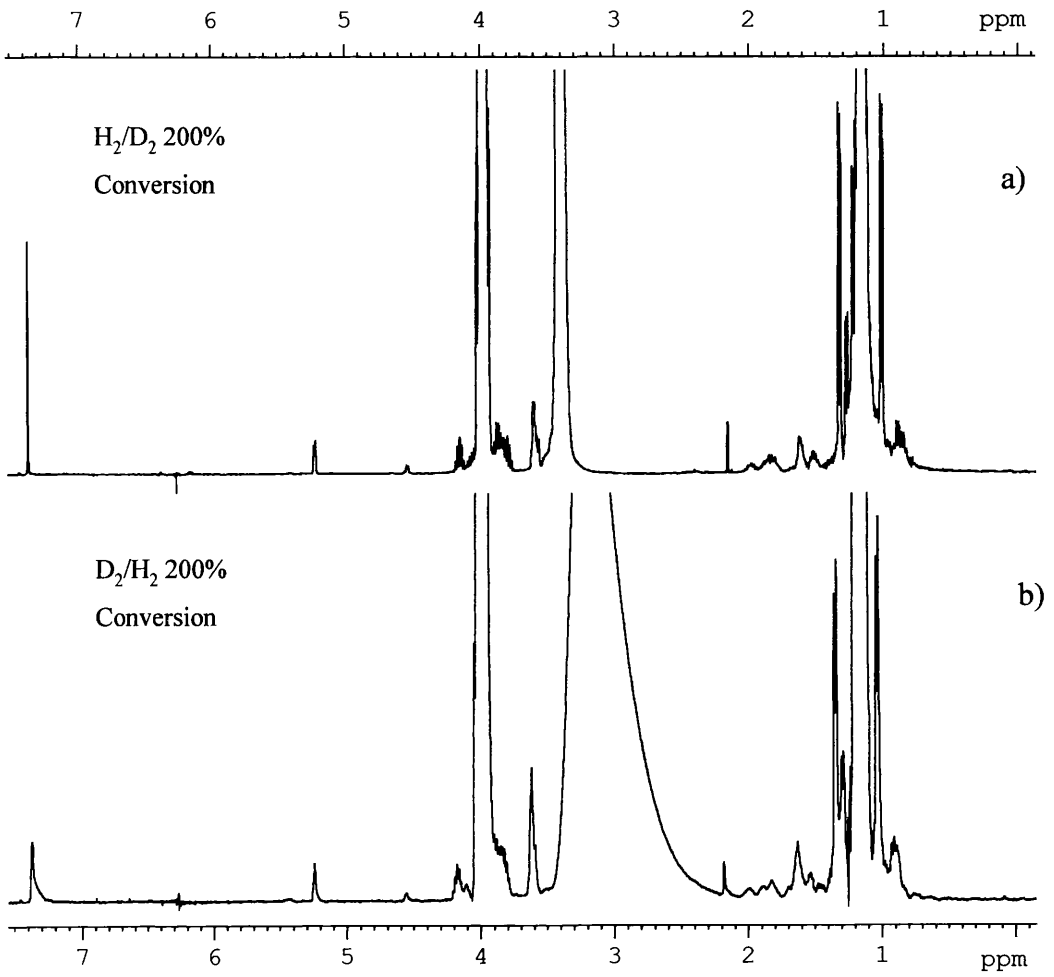
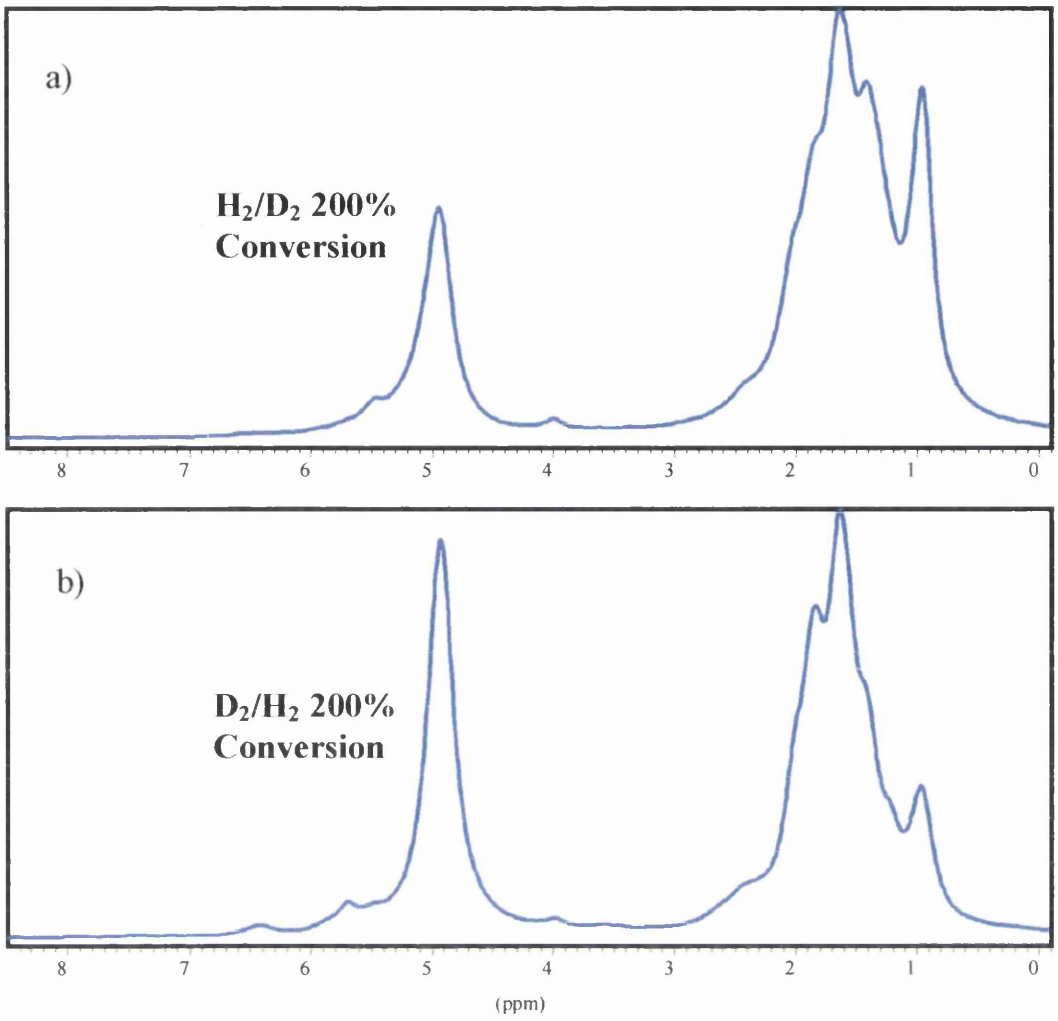


Figure 6.5.6 ^{2}D spectra for H_2/D_2 and D_2/H_2 elevated pressure reactions



6.6 SUMMARY OF MASS-SPECTRA DATA FROM THE ELEVATED PRESSURE MECHANISM REACTIONS

To help try and reinforce the observations made from the elevated pressure mechanism reactions when utilising ^{2}D NMR and ^{1}H NMR spectra, it was decided to analyse samples from the elevated pressure mechanism series of experiments using GC-MS. The use of D_2 gas in most of the elevated pressure mechanism experiments, either for complete hydrogenation or for part hydrogenation of the reaction, should be detectable by a gain in mass for the species that have D atom(s) incorporated into them, using GC-MS analysis. GC-MS analysis can also be used to try to confirm how many D atoms are present in the 3g, 4g and 5g positions in iso-propoxytetrahydrofuran. If there are three D atoms present in iso-propoxytetrahydrofuran, then from the previous ^{1}H NMR and ^{2}D NMR spectra they are very likely to be in the 3g and 4g (two D atoms) of the iso-propoxytetrahydrofuran respectively. The spectra displayed are representative spectra for the different elevated pressure reactions conducted for this chapter. All the mass-spectra in this section are representative of reaction products at 200% conversion.

Figure 6.6.1 shows the mass-spectra taken from the four different elevated pressure reaction types. The spectra are what would be expected for 2-butyne-1,4-diol, with the spectra agreeing with the standard spectra from the computer based mass-spectra reference library. There is no evidence in any of the spectra that any of the 2-butyne-1,4-diol reagent in any of the elevated pressure mechanism reactions has undergone exchange of their 1a protons with deuterium.

Figure 6.6.2 displays a mass-spectrum for *cis*-2-butene-1,4-diol taken from the four main types of elevated pressure reactions. Figure 6.6.2 a) is a mass-spectrum for *cis*-2-butene-1,4-diol from the H_2 elevated pressure reaction, it agrees with the standard spectrum from the computer based mass-spectra reference library. Figure 6.6.2 b) displays a typical mass-spectrum for *cis*-2-butene-1,4-diol taken from the D_2 elevated pressure mechanism. The main

differences between this spectrum and Figure 6.6.2 a) is that mass 59, 71 and 72 have replaced mass 57, 69 and 70 respectively. This increase in the mass for the fragments ties into the two 2b protons in *cis*-2-butene-1,4-diol being deuterium atoms instead of hydrogen atoms, because the 2-butyne-1,4-diol is being selectively hydrogenated with D_2 gas rather than H_2 gas as it is in the H_2 elevated pressure mechanism experiment. Figure 6.6.2 d) displays a mass-spectrum for *cis*-2-butene-1,4-diol taken from a D_2/H_2 elevated pressure mechanism reaction. Again mass 57, 69 and 70 have been replaced with 59, 71 and 72. This as in the previous spectrum on the top of the page, shows that the species present at 2b are D instead of H from the selective hydrogenation of 2-butyne-1,4-diol with D_2 gas. For any of the reactions that employed D_2 gas to hydrogenate, either initially or throughout the course of the reaction, there is no evidence of the *cis*-2-butene-1,4-diol gaining any more than two D atoms, i.e. there is no complex exchange of protons.

Figure 6.6.2 c) is a mass-spectrum for *cis*-2-butene-1,4-diol taken from the H_2/D_2 elevated pressure reaction. The splitting pattern for the spectrum is almost identical to that for the H_2 elevated pressure reaction, indicating that when the 2-butyne-1,4-diol gain two protons or two deuterium atoms to become *cis*-2-butene-1,4-diol, the atoms it gains are the ones it keeps even after the switching in of the other isotope in the mixed isotope experiments. In other words, hydrogen addition occurs in a discrete forward manner. There is no molecular ion present in any of the *cis*-2-butene-1,4-diol spectra detailed, although this may be overcome be expanding the range of available masses displayed on the x-axis scale.

Figure 6.6.3 a) displays a mass-spectrum for butane-1,4-diol taken from a H_2 elevated pressure reaction. The spectrum for butane-1,4-diol agrees with the spectrum from the computer based mass-spectra reference library . Figure 6.6.3 b) displays a mass-spectrum for butane-1,4-diol taken from a D_2 elevated pressure reaction. The main differences between this spectrum and the previous spectrum displayed are that mass 57 and 71 have been replaced with mass 60 and 75 respectively. This is consistent with the 2c positions in the butane-1,4-diol having four D atoms instead of four H atoms. Four H

atoms at the 2c position would be consistent with the selective hydrogenation of 2-butyne-1,2-diol to butane-1,4-diol using H_2 gas. The four D atoms at the 2c positions are consistent with the selective hydrogenation of 2-butyne-1,4-diol to butane-1,4-diol (going through *cis*-2-butene-1,4-diol) using D_2 gas.

Figure 6.6.3 c) displays a mass-spectrum for butane-1,4-diol taken from a H_2/D_2 elevated pressure mechanism reaction. Unlike the previous spectrum, the spectrum does not detail butane-1,4-diol as being fully D atoms in the 2c positions. In this spectrum there is evidence of one (mass 58 and 72), two (mass 59 and 73), three (mass 60 and 74), four (mass 61 and 75) and zero (mass 57 and 71) D atoms in the 2c positions. This is consistent with the H_2 gas being switched to D_2 gas for the end of the H_2/D_2 elevated pressure mechanism reaction, leading to a variety of numbers of D atoms in the 2c positions. Figure 6.6.3 d) displays a mass-spectrum for butane-1,4-diol taken from a D_2/H_2 elevated pressure reaction. This spectrum differs again from the Figure 6.6.3 c). There is evidence in this spectrum of one (mass 58), two (mass 59 and 73), three (mass 60 and 74) and four (mass 75) D atoms at the 2c positions. This is consistent with the D_2 gas being switched to H_2 gas for the end of the D_2/H_2 elevated pressure mechanism reaction, leading to a variety of numbers of D atoms in the 2c positions. The spread of numbers of D atoms present in the butane-1,4-diol spectra helps illustrate that there is a possibility of there being residual H_2 left in the H_2/D_2 elevated pressure mechanism reaction, and residual D_2 left in the D_2/H_2 elevated pressure mechanism reaction, after the switching of the isotopes (either in the reaction solution or on the catalyst surface).

It is not however conclusive evidence of scrambling (more evidence is required), although scrambling seems likely. It is possible however, that the main factor for the spread of masses in the two experiments is because the reaction products are derived from *cis*-2-butene-1,4-diol, and the fact that the isotopes have been switched before the complete formation of *cis*-2-butene-1,4-diol. There seems to be a degree of reversibility in the reaction pathways. We see a single pathway up to *cis*-2-butene-1,4-diol, implying a forward irreversible pathway up to *cis*-2-butene-1,4-diol, when cis-2-butene-1,4-diol is

re-adsorbed onto the catalyst and forms the other products, it seems that some degree of reversibility in the reaction pathways can occur. There is no molecular ion present in any of the butane-1,4-diol spectra detailed, for the same reasons as detailed before.

Figure 6.6.4 a) displays a mass-spectrum for butanol taken from a H_2 elevated pressure reaction, the spectrum agrees with the computer based mass-spectra reference library. Figure 6.6.4 b) displays a mass-spectrum for butanol taken from the H_2/D_2 pressure mechanism reaction. The main differences between this spectrum and Figure 6.6.4 a) are the spread of masses around mass 45 and 56. It is clear form this spectrum that butanol can be produced from a number of sources during the course of the selective hydrogenation of 2-butyne-1,4-diol, if it is allowed to carry onto 200% (*i.e.* full) conversion. Masses 44, 46 and 59 indicate that the three D atom form of butanol is the most common for this type of reaction set-up. We can also observe the one (mass 41, 44, 46 and 57), two (mass 43, 45, 47 and 58) and the four (mass 45, 47 and 49) D atoms in the butanol backbone. There is also the possibility of five and six D atoms in the butanol backbone. The multiple possible sources of butanol from the various reaction pathways coupled with the fact that the H_2 gas was switched to D_2 gas for the end of the H_2/D_2 elevated pressure reaction allow for the many forms of butanol observed (due to scrambling). This is further evidence of reversible reaction steps that exist from *cis*-2-butene-1,4-diol onwards.

Figure 6.6.4 c) displays a mass-spectrum for butanol taken from the D_2/H_2 elevated pressure reaction. The main differences between this spectrum and Figure 6.6.4 a) are the spread of masses around mass 45 and 56 again. It is clear form this spectrum that butanol can be produced from a number of sources during the course of the selective hydrogenation of 2-butyne-1,4-diol, if it is allowed to carry onto 200% (*i.e.* full) conversion. Masses 44, 46 and 59 indicate that the three D atom form of butanol is the most common for this type of reaction set-up. We can also observe the one (mass 41, 44, 46 and 57), two (mass 43, 45, 47 and 58) and the four (mass 45, 47 and 49) D atoms in the butanol backbone. There is also the possibility of five and six D atoms in the butanol backbone. The multiple possible sources of butanol from the various

reaction pathways coupled with the fact that the D_2 gas was switched to H_2 gas for the end of the D_2/H_2 elevated pressure reaction allow for the many forms of butanol observed. As in the previous spectrum it is difficult to fully quantify the amounts of the different butanol species present because of the number of possibilities for different species and the amount of spectral overlap. As before, there is no molecular ion present in any of the butanol spectra detailed.

Figure 6.6.5 a) displays a mass-spectrum for *cis*-crotyl alcohol taken from the H_2 elevated pressure reaction. The spectrum for *cis*-crotyl alcohol agrees with the standard spectrum from the computer based mass-spectra reference library. There are no other mass-spectra for *cis*-crotyl alcohol available in the experimental data obtained due to the low levels of it produced during the reaction, and the amount left at 200% conversion. Figure 6.6.5 d) displays a mass-spectrum for *trans*-crotyl alcohol taken from the H_2 elevated pressure reaction. The spectrum for *trans*-crotyl alcohol agrees the standard spectrum from the computer based mass-spectra reference library. There are no other mass-spectra for *trans*-crotyl alcohol available for the same reasons as for *cis*-crotyl alcohol.

Figure 6.6.5 a) displays a mass-spectrum for 3-buten-1-ol taken from H_2 elevated pressure mechanism reaction. The spectrum for 3-buten-1-ol agrees with the standard spectrum from the computer based mass-spectra reference library. Figure 6.6.5 b) displays a mass-spectrum for 3-buten-1-ol taken from D_2 elevated pressure mechanism reaction. The spectrum shows mass 53, 71 and 72 being replaced with mass 57, 74 and 75 respectively, indicating that the 3-buten-1-ol has three D atoms in the backbone. Mass 57 has been replaced with mass 59 which would indicate two D atoms in the 3-butene-1-ol backbone after it has been broken down in the MS. This spectrum is consistent with iso-proproxytetrahydrofuran having three D atoms between positions 3g and 4g (two in position 4g). There are no other mass-spectra for 3-buten-1-ol available in the experimental data obtained due to the low levels of it produced during the reaction, and the amount left at 200% conversion.

Figure 6.6.6 a) displays a mass-spectrum for iso-propoxytetrahydrofuran taken from a H_2 elevated pressure mechanism reaction. The spectrum for iso-propoxytetrahydrofuran agrees with what has been observed in previous investigations. Figure 6.6.6 b) displays a mass-spectrum for iso-propoxytetrahydrofuran taken from a D_2 elevated pressure mechanism reaction. The main differences with the spectrum and the one displayed previously are that mass 71, 88, 115 and 130 have been replaced with 74, 91, 118 and 133 respectively. This increase in mass is consistent with there being three D atoms on the furan ring. The other masses that appear in the spectrum are a consequence of the pathways available to the formation of iso-propoxytetrahydrofuran (e.g. *cis* and *trans*-crotyl alcohol going through a central intermediate as proposed in the reaction mechanism and the possibility of isomerisation between 3-buten-1-ol and *cis* and *trans*-crotyl alcohol). This shows some degree of reversibility in the reaction pathways.

Figure 6.6.6 c) displays a mass-spectrum for iso-propoxytetrahydrofuran taken from the H_2/D_2 elevated pressure reaction. In this spectrum mass 71 is joined by mass 72 (as the second most populated state of furan ring), mass 115 is joined by mass 116 (with the abundance of mass 116 being greater). The main form of furan ring that is observed in the reaction is one with one D atom incorporated. Again the other masses that appear in the spectrum are a consequence of the pathways available to the formation of iso-propoxytetrahydrofuran (e.g. *cis* and *trans*-crotyl alcohol going through a central intermediate as proposed in the reaction mechanism). The other possible routes for the formation of iso-propoxytetrahydrofuran coupled with that fact the H_2 gas was switched to D_2 gas for the end of the H_2/D_2 elevated pressure mechanism reaction allow for the forms of iso-propoxytetrahydrofuran observed. The switch illustrates that the path from 2-butyne-1,4-diol to *cis*-2-butene-1,4-diol is one way, the reaction intermediate that is required to form iso-propoxytetrahydrofuran only gains another hydrogen atom after it is formed from *cis*-2-butene-1,4-diol.

Figure 6.6.6 d) displays a mass-spectrum for iso-propoxytetrahydrofuran taken from a D_2/H_2 elevated pressure reaction. In this spectrum mass 71 is

greater than mass 73 (as the second most populated state of furan ring), mass 115 is replaced by mass 117, when compared to Figure 6.6.6 b) for the H_2/D_2 elevated reaction for iso-propoxytetrahydrofuran, it shows that two hydrogen atoms are added to 2-butyne-1,4-diol to from *cis*-2-butene-1,4-diol. The main form of furan ring that is observed in the reaction is one with two D atoms incorporated. Again the other masses that appear in the spectrum are a consequence of the pathways available to the formation of iso-propoxytetrahydrofuran (e.g. *cis* and *trans*-crotyl alcohol likely to be going through a central intermediate as proposed in the reaction mechanism).

The switching of the different isotopes of hydrogen during the course of the reaction helps to highlight the differing pathways available for the formation of iso-propoxytetrahydrofuran and confirm that there should be common reaction intermediate(s) that can explain the selectivities and product yields formed during the reaction process.

It has been previously stated that 3-buten-1-ol is the precursor to the formation of iso-proproxytetrahydro furan, the intermediate associated with 3-buten-1-ol can have one proton added and then, in the presence of propan-2-ol go onto form iso-propoxytetrahydrofuran. The source of this proton is determined by whether or not H_2 gas or D_2 gas has been used to hydrogenate the reaction or a mixture of both has been employed. In a reaction that only uses H_2 gas to hydrogenate the mass-spectra would be expected to show a peak at mass 71 associated with the furan ring component of the iso-propoxytetrahydrofuran. In a reaction that only uses D_2 gas to hydrogenate the mass-spectra would be expected to show a peak at mass 74 associated with the furan ring component of the iso-propoxytetrahydrofuran. This illustrates that three D atoms in positions 3g, 4g and 5g of the furan ring, the spread of masses around mass 74 are indicative of the many reaction pathways available in the reaction mechanism.

For a reaction that has employed H_2 gas to hydrogenate, up to the point where most of the *cis*-2-butene-1,4-diol has been formed, and then the gas has been switched to D_2, it is expected that a peak at mass 72 would replace the peak at

mass 71. Even though the iso-propoxytetrahydrofuran still consists of the same number atoms as before, the gain of one D atom is required on the 3-buten-1-ol intermediate to produce iso-propoxytetrahydrofuran, the intermediate having no D atoms present, because it was derived from *cis*-2-butene-1,4-diol with no deuterium atoms present in its structure. For a reaction that has employed D_2 gas to hydrogenate, up to the point where most of the *cis*-2-butene-1,4-diol has been formed, and then the gas has been switched to H_2, it is expected that a peak at mass 73 would replace the peak at mass 71. Even though the iso-propoxytetrahydrofuran still consists of the same number atoms as before, the gain of one H atom is required on the 3-buten-1-ol intermediate to produce iso-propoxytetrahydrofuran, the intermediate having two D atoms present, because it was derived from *cis*-2-butene-1,4-diol with two deuterium present in its structure. The reactions that used both H_2 gas and D_2 gas to hydrogenate, help bring into focus the probable form of the reaction mechanism.

Figure 6.6.1 Mass spectra for 2-butyne-1,4-diol for the mechanism reactions

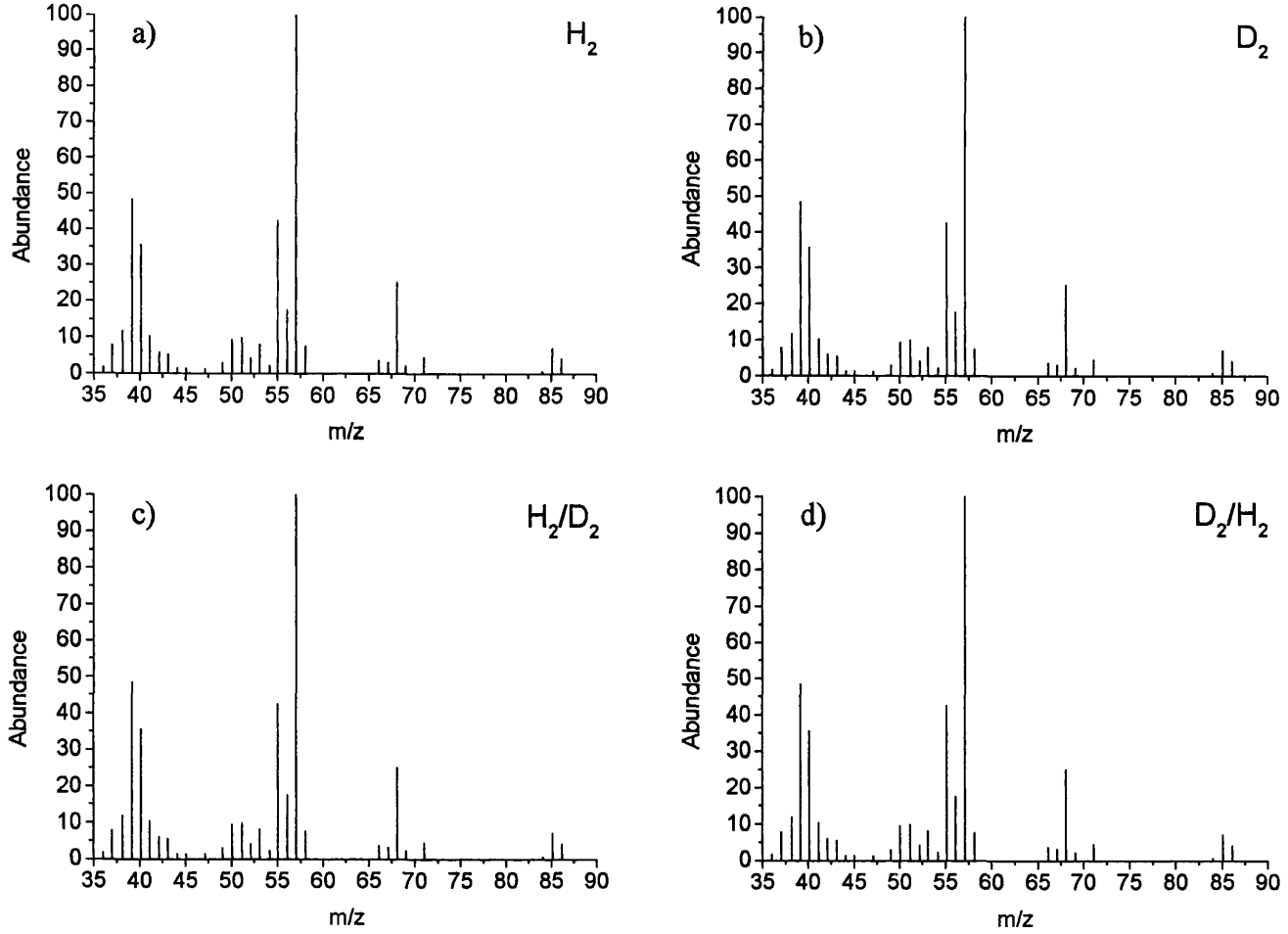


Figure 6.6.2 Mass spectra for *cis*-2-butene-1,4-diol for the mechanism reactions

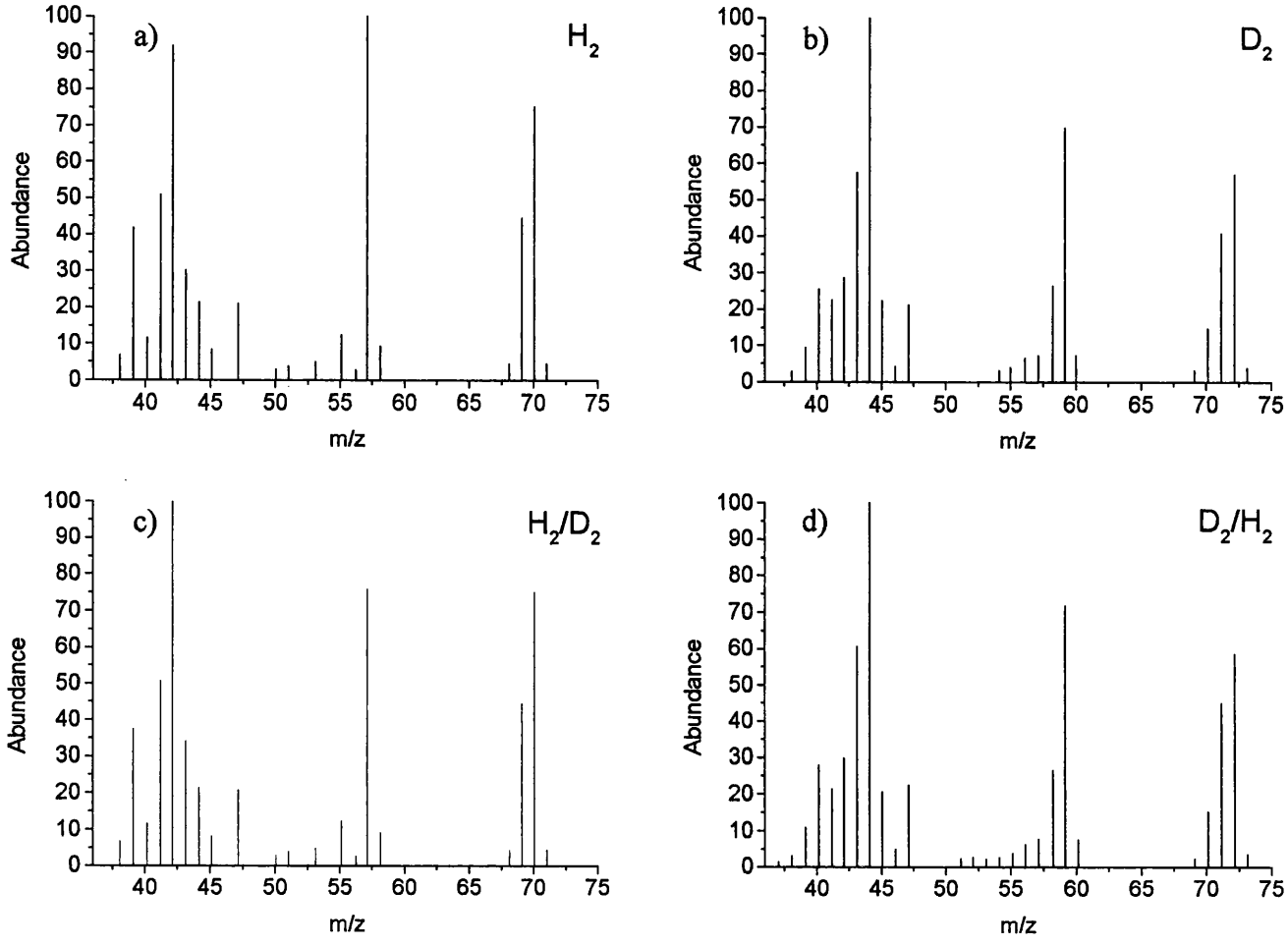


Figure 6.6.3 Mass spectra for butane-1,4-diol for the mechanism reactions

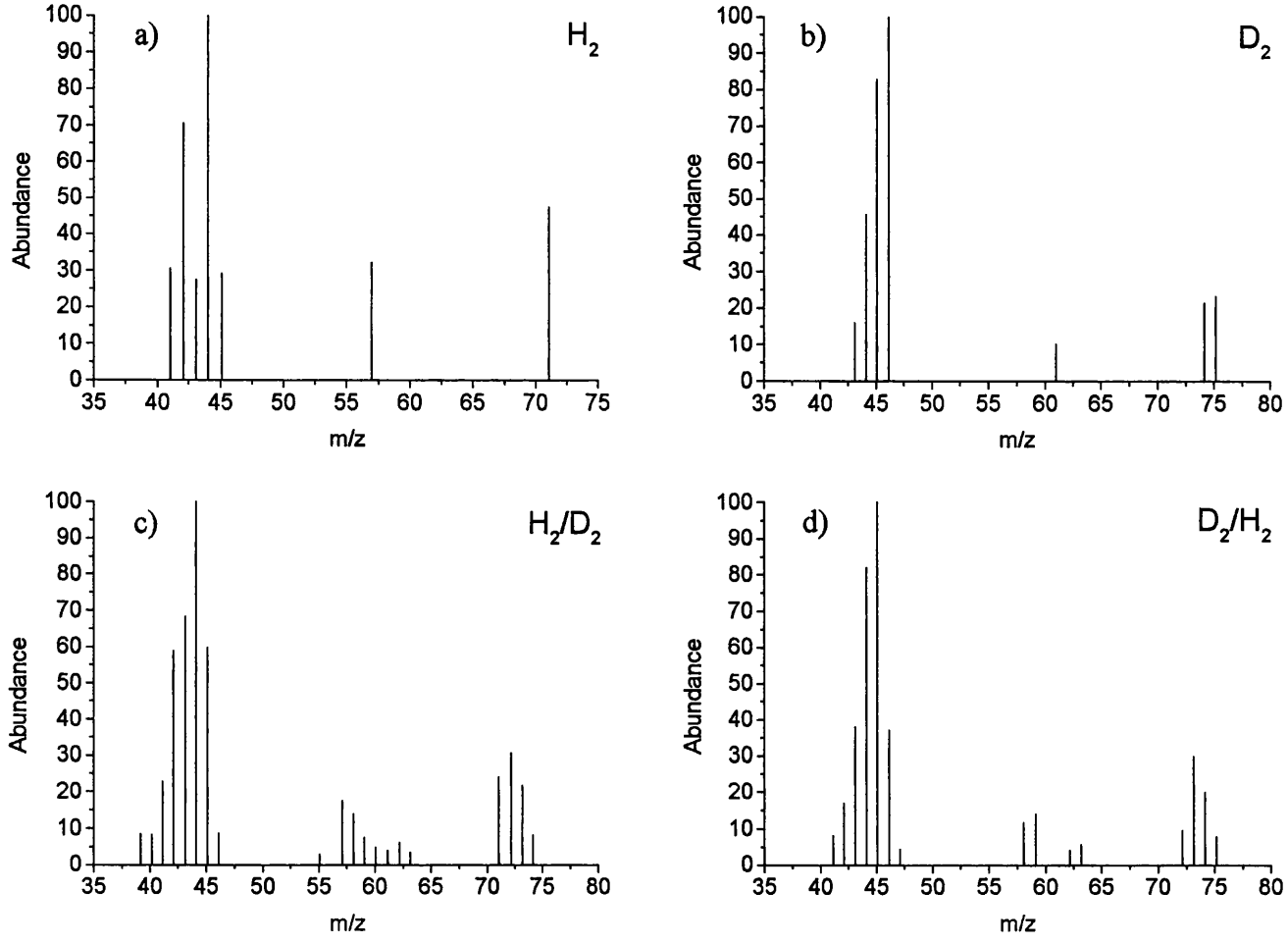


Figure 6.6.4 Mass spectra for butanol for the mechanism reactions

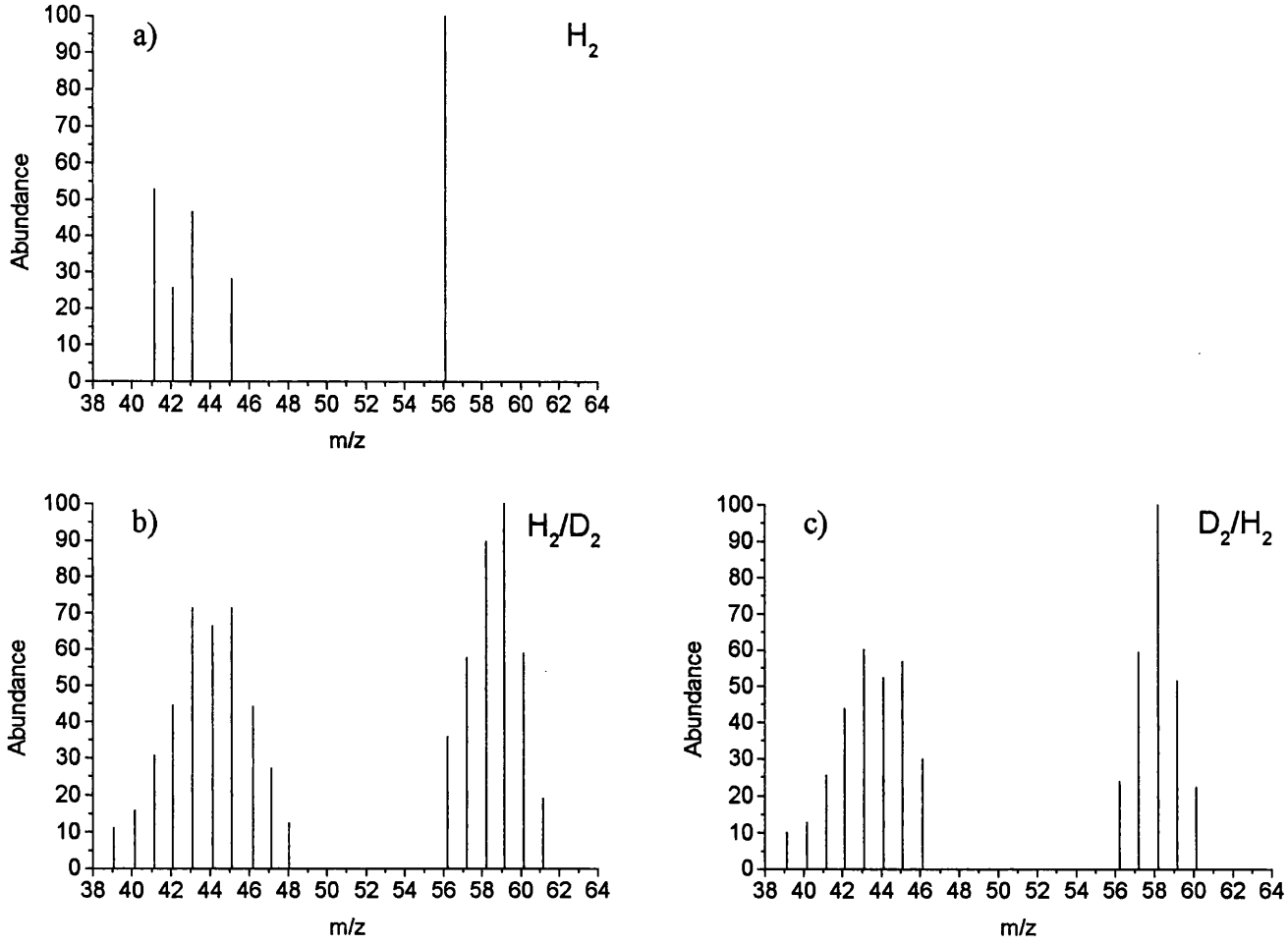


Figure 6.6.5 Mass spectra for 3-butene-1-ol, *cis* and *trans*-crotyl alcohol for the mechanism reactions

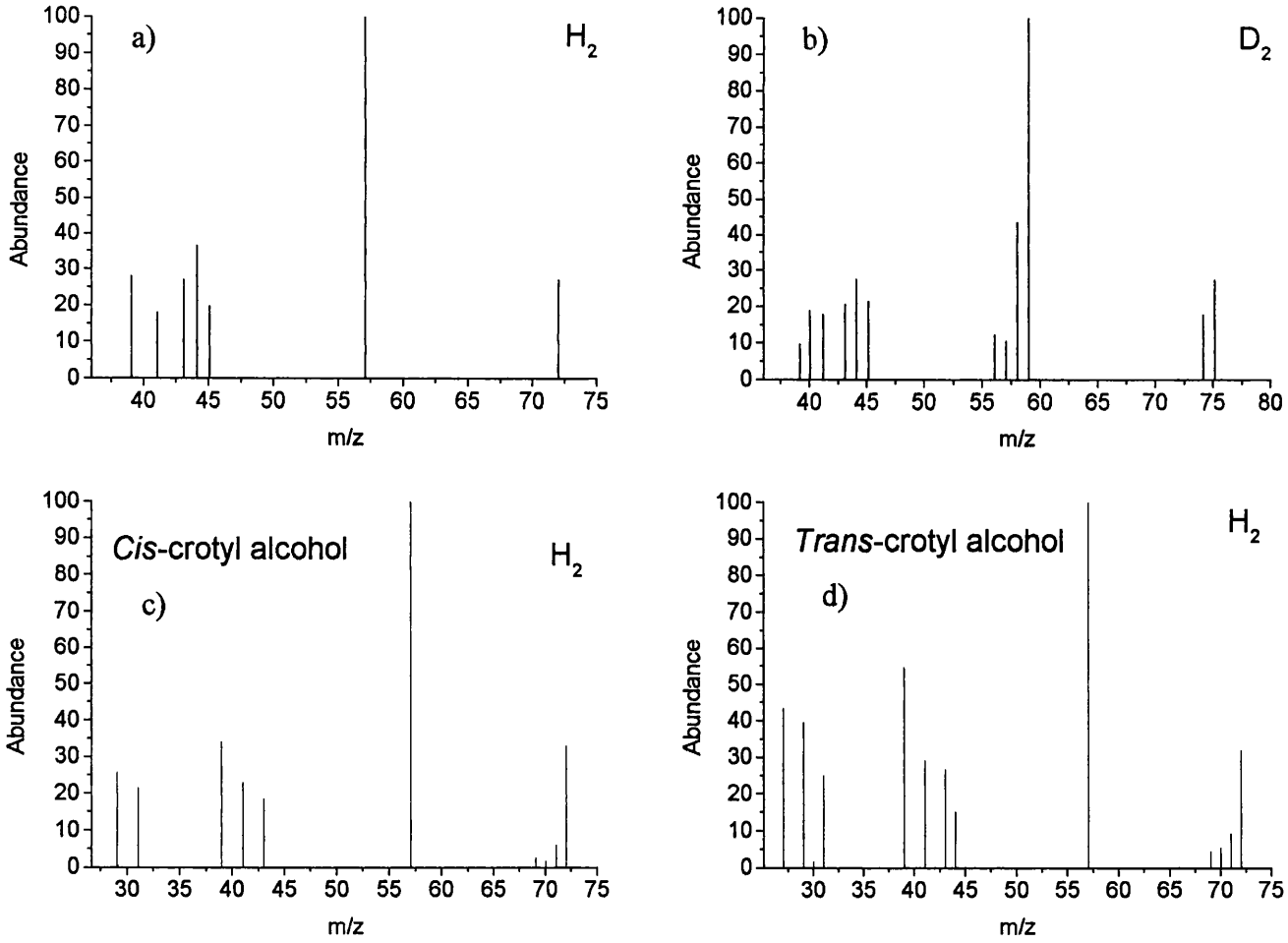
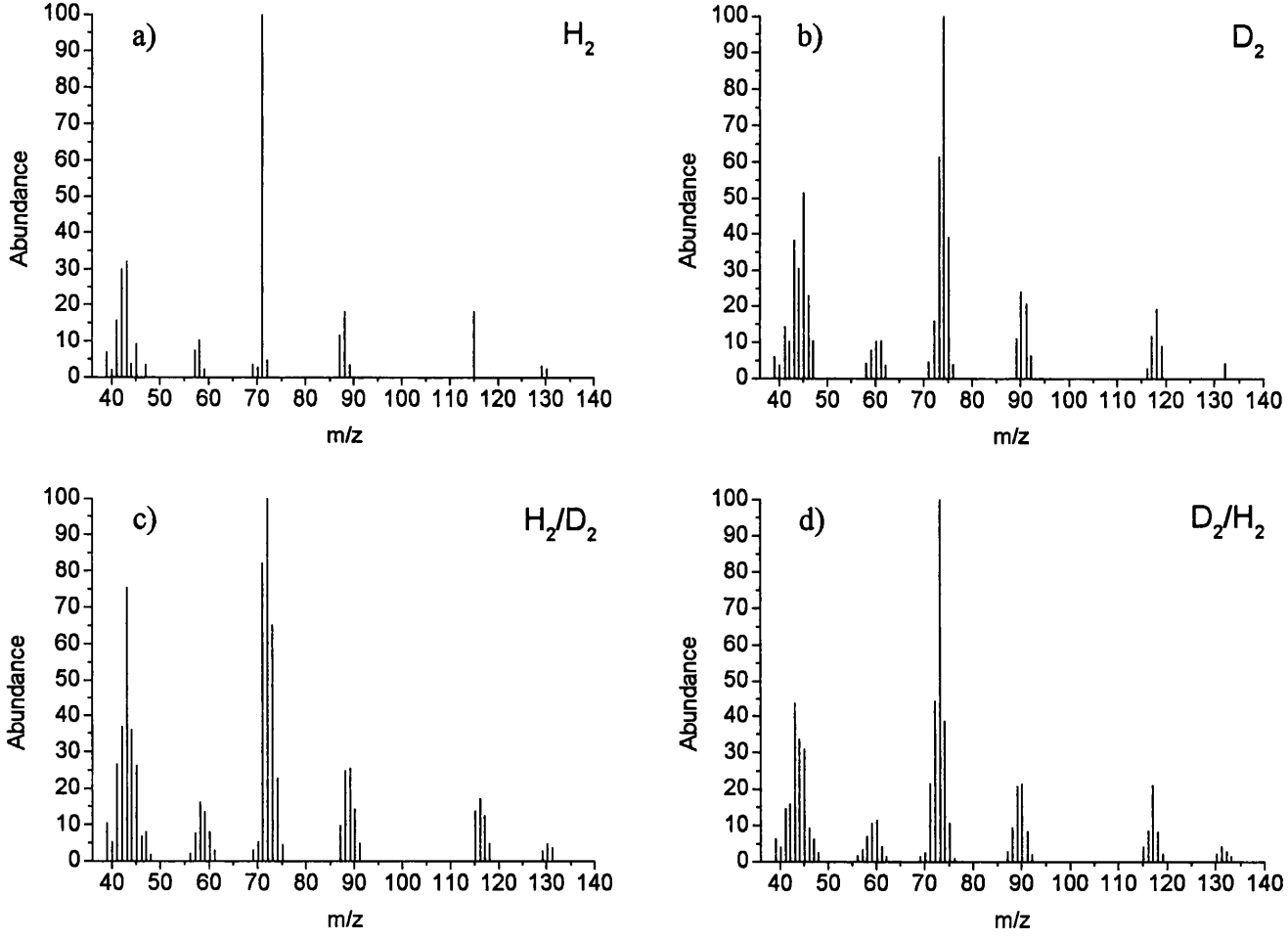


Figure 6.6.6 Mass spectra for iso-propoxytetrahydrofuran for the mechanism reactions



6.6.1 SUMMARY FOR SECTION 6.5 AND 6.6.

- ^{1}H and ^{2}D NMR in combination with isotope switching have successfully been used to follow the reaction to completion.

- ^{1}H and ^{2}D NMR confirm that D atoms can be added consecutively to the adsorbed 2-butyne-1,4-diol species.

- With the use of GC-MS, it is possible to determine the exact amount of H and or D atoms present in the reaction species at any time throughout the reaction.

- There are only three D atoms gained to form iso-propoxytetrahydrofuran in total when D_2 gas is used throughout the reaction. Two of which come from the initial hydrogenation of the adsorbed C-4 species, there is evidence of a concerted ring closure to form iso-propoxytetrahydrofuran.

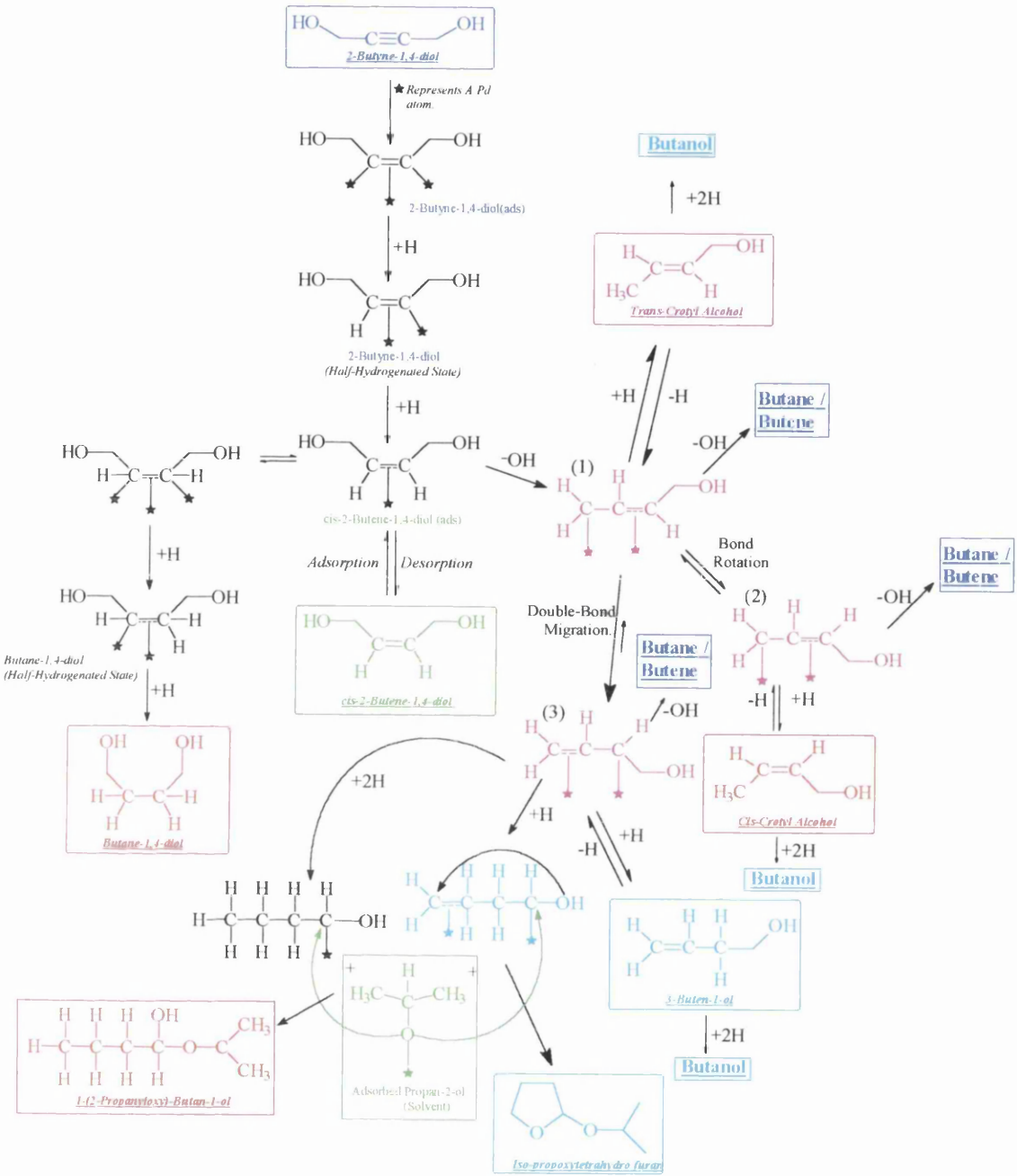
- The reaction steps from the adsorbed 2-butyne-1,4-diol species to the adsorbed *cis*-2-butene-1,4-diol species are essentially in one direction. There is no evidence of any non-surface bound deuterated 2-butyne-1,4-diol.

6.6.2 REACTION MECHANISM

All the reactions that have been detailed in this chapter, and indeed in this entire study, point towards the possibility of an overall reaction mechanism being able to explain the trends observed during the reactions. The experiments detailed in this chapter endeavour to probe the possible reaction pathways by the combination of targeted ^{1}H and ^{2}D isotope switching using both NMR and GC-MS analysis. The purpose of these experiments was to attempt to develop the existing reaction scheme into a plausible reaction mechanism through the elucidation of reaction pathways.

By taking into account these observations and those observed from experiments detailed in previous chapters it has been possible to condense the observed reaction profiles into an overall plausible reaction mechanism. Figure 6.6.2 shows a condensed format for the overall reaction mechanism. Exploded views of the reaction mechanism are detailed in Section 6.7. It is better to view the overall mechanism initially before examining the exploded views in more detail.

Figure 6.6.2 Summarised reaction mechanism



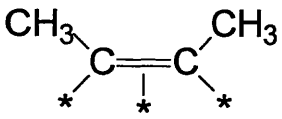
6.7 EXPLAINATION FOR POSTULATED REACTION MECHANISM

The best way to try to explain the reaction mechanism is to split it into four separate figures. To this end, Figures 6.7.2, 6.7.3, 6.7.4 and 6.7.5 have an exploded representation of the overall reaction mechanism. All the reaction mechanism figures in this section have the same common backbone. The basic structure of the mechanism is based on work conducted in our laboratories on 2-butyne hydrogenation employing a 1% Pd/SiO_2 catalyst [10], and work published in the literature on *n*-butene hydrogenation and isomerisation [11].

In reaction mechanism Figure 6.7.2 the first thing that should be considered is 2-butyne-1,4-diol. 2-butyne-1,4-diol has to be adsorbed onto the catalyst surface. The most likely route for this to occur is through a 2,3 di-σ/π bound 2-butyne-1,4-diol species. To do this 2-butyne-1,4-diol must undergo a change from sp hybridisation to sp^2 hybridisation, *i.e.* the triple bonded 2-butyne-1,4-diol changes to something nearer a double bonded 2-butyne-1,4-diol species so that it can be adsorbed on to an active site on the catalyst surface in a di-σ/π bound type manner.

There are no literature studies that deal with the adsorption of 2-butyne-1,4-diol on a supported palladium catalyst or single palladium crystal. There are a few metal single crystal studies that examine the form of the adsorption of 2-butyne though, on Cu(111) [12, 13], Ni(111) [14] and Pt (111) [15, 16]. More interestingly work carried out on a Pd(100) confirms that a 2,3-di-σ/π bound 2-butyne species is possible with reflection absorption infrared spectroscopy [17]. Kennedy proposed a 2,3-di-σ/π bound 2-butyne species [10], detailed in Figure 6.7.1 below, after comparing his IR assignments with Chesters' *et al* [15].

Figure 6.7.1 Proposed structure for 2,3-di-σ/π bound 2-butyne



If 2-butyne can be adsorbed onto the surface of the catalyst in a 2,3-di-σ/π bound species, then it is likely that 2-butyne-1,4-diol will adsorb in a similar manner as detailed in the reaction mechanism Figures 6.7.2, 6.7.3, 6.7.4 and 6.7.5.

Once the 2-butyne-1,4-diol is adsorbed, the next stage in the reaction mechanism is for 2-butyne-1,4-diol (ads) to gain a hydrogen atom to become the half hydrogenated state of 2-butyne-1,4-diol (through syn-addition of a hydrogen atom). With the gain of another hydrogen atom through syn-addition from the catalyst surface, the half hydrogenated 2-butyne-1,4-diol becomes *cis*-2-butyne-1,4-diol (ads). The *cis*-2-butene-1,4-diol (ads) species can then desorb from the catalyst. This describes the common backbone that is present in all of the reaction mechanism Figures in this section. We can consider this process to be one way from 2-butyne-1,4-diol to *cis*-2-butene-1,4-diol. There is no evidence in any of the reactions that have been detailed in this thesis that *cis*-2-butene-1,4-diol can be converted back to 2-butyne-1,4-diol on the catalyst surface. More importantly however, is the fact that there is no significant hydrogenation of *cis*-2-butene-1,4-diol when there is still 2-butyne-1,4-diol present in the reaction solution. The NMR, GC-MS data from this chapter support the fact that 2-butyne-1,4-diol is converted irreversibly to *cis*-2-butene-1,4-diol during the first stage of the reaction.

The reason for the double arrow in Figure 6.7.2 between *cis*-2-butene-1,4-diol (ads) and *cis*-2-butene-1,4-diol, is to show that the *cis*-2-butene-1,4-diol that is formed during the course of the reaction can be re-adsorbed onto the catalyst surface, after all the 2-butyne-1,4-diol has been hydrogenated. All the "side products" come from *cis*-2-butene-1,4-diol, rather than straight from 2-butyne-1,4-diol as shown by the reactions in Sections 5.2, 5.3, 5.6, 5.7 and

6.3, where we see little of the "side products" while there is still 2-butyne-1,4-diol present in the reaction solution.

Once adsorbed onto the catalyst the *cis*-2-butene-1,4-diol can go through a similar series of steps to form butane-1,4-diol (*i.e.* syn-addition of hydrogen atoms). The *cis*-2-butene-1,4-diol first becomes *cis*-2-butene-1,4-diol (ads) (bound in a 2,3-di-σ/π type species), then it gains a hydrogen atom, before gaining another hydrogen atom and desorbing form the catalyst as butane-1,4-diol.

The other reaction pathway that is detailed on Figure 6.7.2 is the formation of 2-butyne-1-ol form 2-butyne-1,4-diol. The formation of 2-butyne-1-ol has only been observed when the 1% Pd/Al_2O_3 (chloride precursor) catalyst has been employed. 2-butyne-1-ol is likely to originate form the half hydrogenated state of 2-butyne-1,4-diol. With the loss of a hydroxyl group and the gain of a hydrogen atom, 2-butyne-1-ol can be produced.

The main purpose of reaction Figure 6.7.3 is to detail the possible formation of *cis* and *trans*-crotyl alcohol and 3-buten-1-ol. The formation of the aforementioned products can be traced to the adsorbed *cis*-2-butene-1,4-diol. *Cis*-2-butene-1,4-diol (ads) through the loss of an hydroxyl group, can go on to form one of the reaction intermediates labelled 1,2 and 3. Intermediates 1,2 and 3 can be considered as a central hub through which most of the observed reaction products can be formed. We have evidence from the reactions carried out in Section 5.2, but more importantly the reactions conducted for Section 5.8 that it is possible for the isomerisation between *cis* and *trans*-crotyl alcohol and 3-buten-ol to occur. The isomerisations occur through inter-conversions of the adsorbed intermediate states. There is literature evidence that states that noble metals can cause the isomerisation [11, 18] of adsorbed species and the double bond migration that is required for the formation of 3-buten-ol. Intermediates 1,2 and 3 can gain another hydrogen atom to form *cis*-crotyl alcohol, *trans*-crotyl alcohol and 3-buten-1-ol respectively.

The purpose of Figure 6.7.4 is to outline some of the possible routes to the formation of butanol through intermediates 1,2 and 3. The GC-MS data for butanol with the D_2/H_2 reactions shows that a butanol molecule can have up to six deuterium within it (Figure 6.6.4 b)), the range of other masses in the spectra illustrate that scrambling of the deuterium/hydrogen atoms can occur. One possible mechanism for the scrambling of the deuterium within butanol is the isomerisation and inter-conversion of the reaction intermediates 1,2 and 3. With the of the other hydroxyl group, reaction intermediates 1,2 and 3 can go on to form butane and butene, the cause of the mass imbalance for the reactions that employ the 1% Pd/C catalyst with propan-2-ol. Interestingly with the reaction that were conducted with the mono-substituted alkynes and 3-buten-1-ol with the 1% Pd/C catalyst, the mass balance was more complete than the other reactions that employed the 1% Pd/C catalyst and propan-2-ol as the reaction solvent. The fact that the mono-substituted and 3-buten-1-ol reaction have a more complete mass balance, would suggest that when the starting material is a diol the loss of the second hydroxyl group for the intermediates 1,2 and 3 are more likely. This may be due to a slight conformational change when the intermediates are derived from the mono-substituted and 3-buten-1-ol.

Like the other reaction mechanism figures, Figure 6.7.5 has the same backbone, from 2-butyne-1,4-diol through to *cis*-2-butene-1,4-diol. The main purpose of Figure 6.7.5 is to try and explain the formation of iso-propoxytetrahydrofuran and its "sister" products hydroxy-tetrahydrofuran and 1-(2-propanyloxy)-butan-1-ol. Hydroxy-tetrahydrofuran is produced in small amounts when distilled water was employed as the reaction solvent instead of propan-2-ol with the 1% Pd/C catalyst (Section 5.10). It is produced in larger amounts in the reaction that employs the 1% Pd/Al_2O_3 catalyst (nitrate precursor), but is consumed during the course of the reaction and converted to iso-propoxytetrahydrofuran. 1-(2-propanyloxy)-butan-1-ol is produced in the elevated pressure reactions in Section 5.2, and in the mono-substituted alcohol reactions in Section 5.8. It is not possible for any of the mono-substituted alcohols to produce iso-propoxytetrahydrofuran, the diol functionality of *cis*-2-butene-1,4-diol is required so that a concerted ring closure can occur to

form iso-propoxytetrahydrofuran, this may be because of a slight conformational change in the intermediates derived form the mono-substituted alcohol reactions detailed in Section 5.8.

With the gain of a hydrogen atom reaction intermediate 3 can go onto form reaction intermediate 4. Reaction intermediate 4 is the intermediate that is required to react with the surface bound propoxy group to form iso-propoxytetrahydrofuran through a concerted ring closure. When distilled water was employed as the reaction solvent, there was no adsorbed propan-2-ol species to form iso-propoxytetrahydrofuran. Therefore, reaction intermediate species 4 goes through a concerted ring closure with surface bound hydroxyl groups to for hydroxytetra-hydrofuran (Section 5.11). When the 1% Pd/Al_2O_3 (nitrate precursor) catalyst was employed, the hydroxyl groups are supplied by the Al_2O_3 support (Figure 5.7.2), the process of concerted ring closure to form hydroxy-tetrahydrofuran will be similar to that involved when distilled water was employed as the reaction solvent. When butanol was employed as the reaction solvent then butoxy-tetrahydrofuran is produced (Section 5.11). Through the used of different solvents, it is possible to invoke a different solvent interaction to produce a different substituted furan.

Employing different solvents and different catalysts can have a profound effect on the reaction profiles and final product distributions that are obtained. If we consider typical ambient pressure reactions, one that employed propan-2-ol and one that employed distilled water as the reaction solvent, we can see that the change in reaction solvent from propan-2-ol to distilled water has halved the rate of hydrogenation (Figures 5.2.1 and 5.11.1 respectively). The reduced rate of hydrogenation when distilled water was employed is due to the competition for active sites on the catalyst surface between 2-butyne-1,4-diol and the distilled water, the distilled water hampers the rate of hydrogenation (Section 5.11). Adsorbed water also narrows the range of possible products that are observed in the final reaction profile. Reaction intermediates 1,2 and 3 are almost fully blocked from formation, leading to a narrower range of products in the final product distribution, and an effectively complete mass

balance, because no butane and butene can be formed. Reaction intermediates 1,2 and 3 are required for substituted furan formation, and distilled water largely prevents their formation, this can account for the small amounts of hydroxy-tetrahydrofuran that are produced when distilled water is employed with the 1% Pd/C catalyst.

Figure 6.7.2: Reaction Mechanism part 1

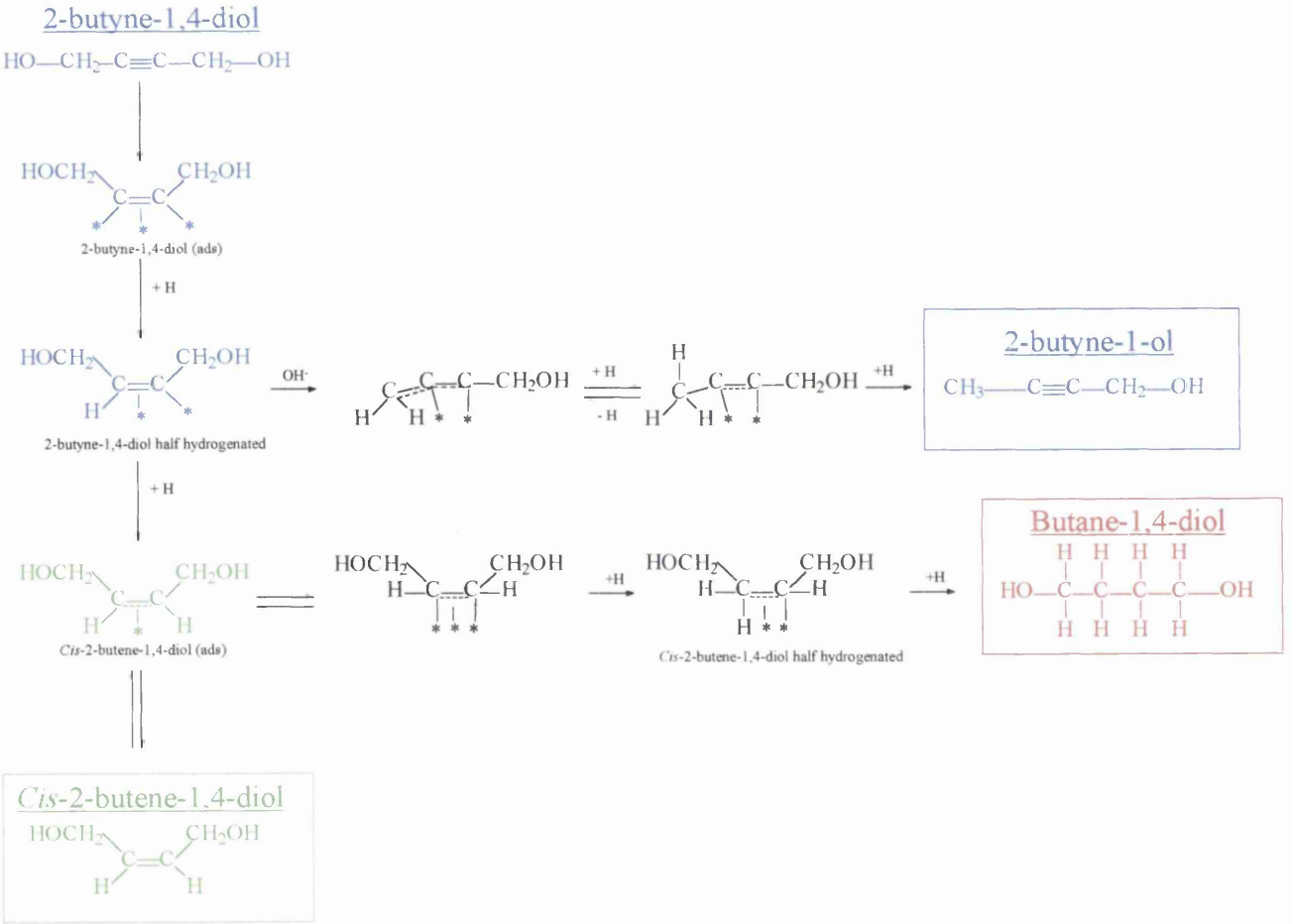


Figure 6.7.3: Reaction Mechanism part 2

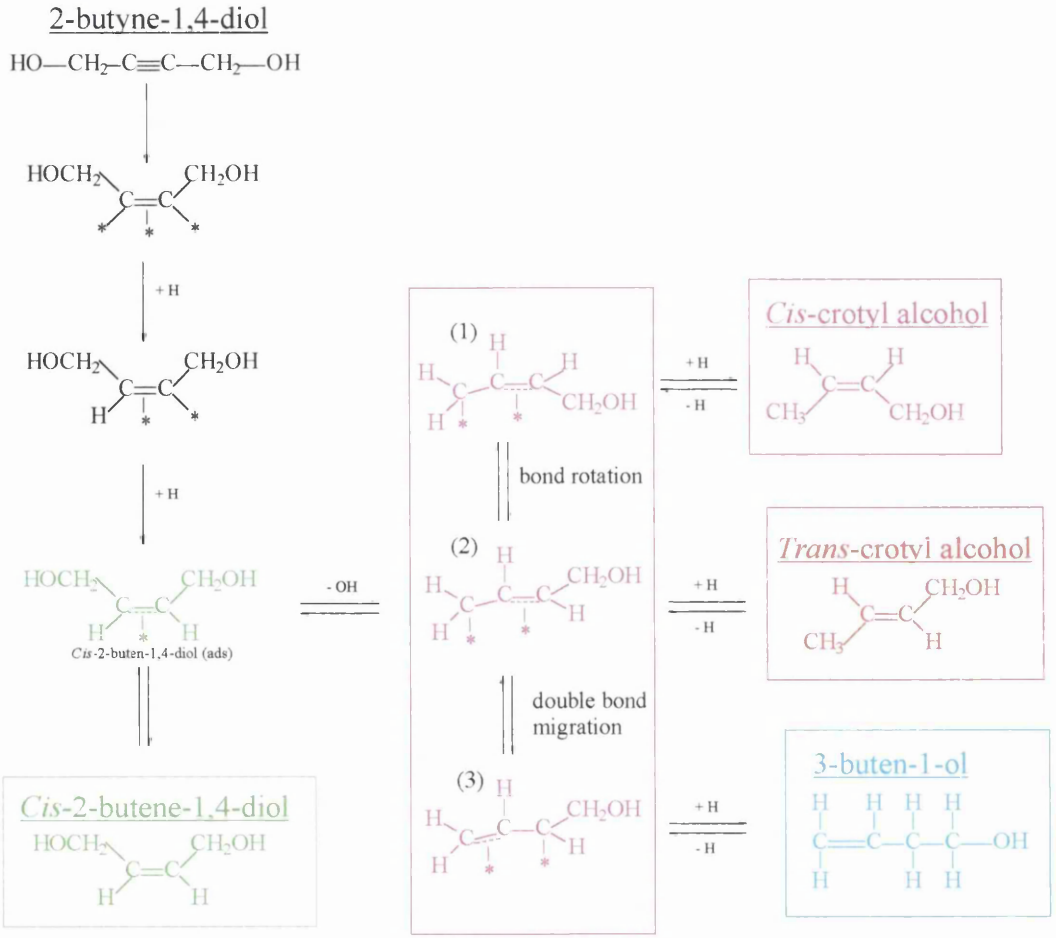


Figure 6.7.4: Reaction Mechanism part 3

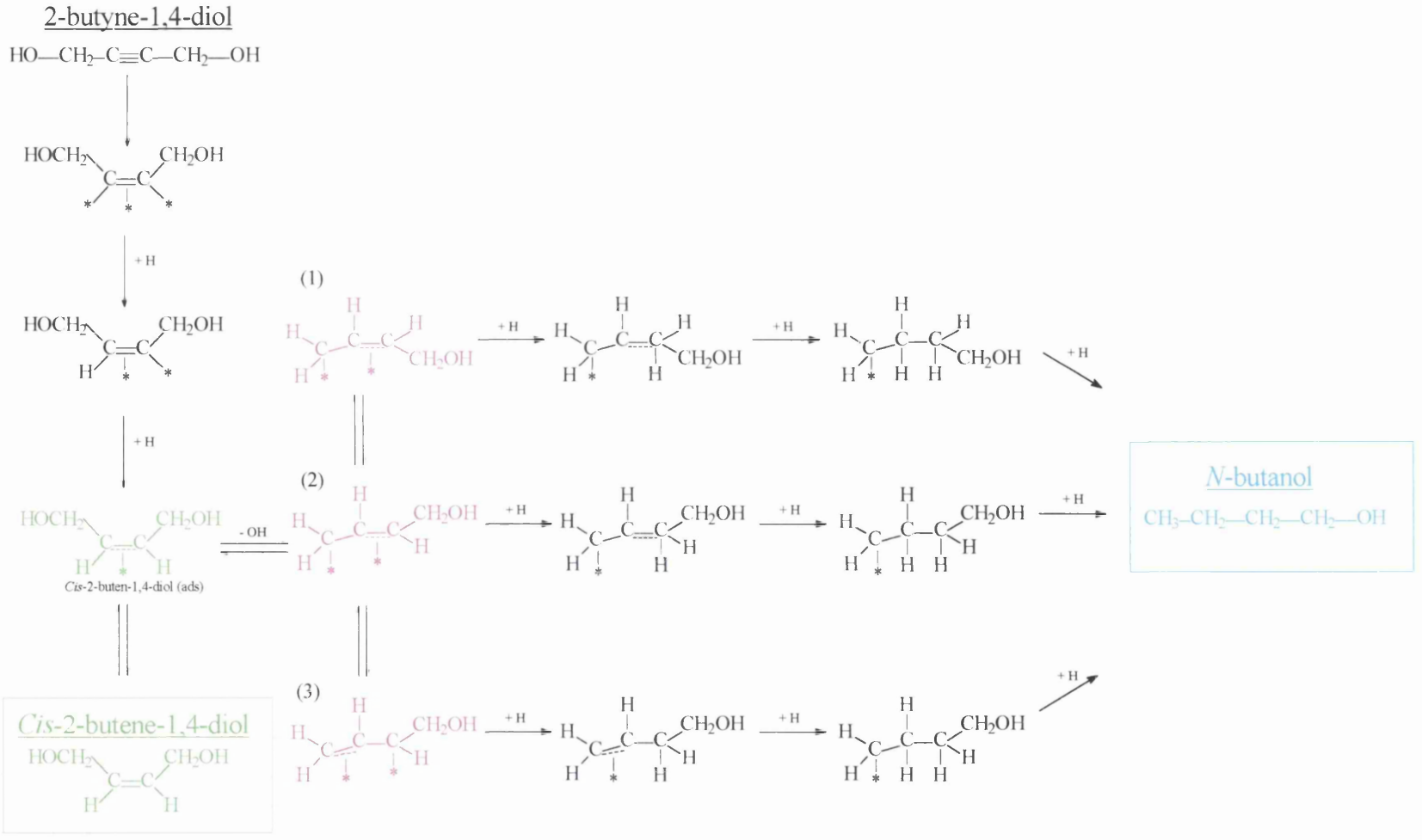
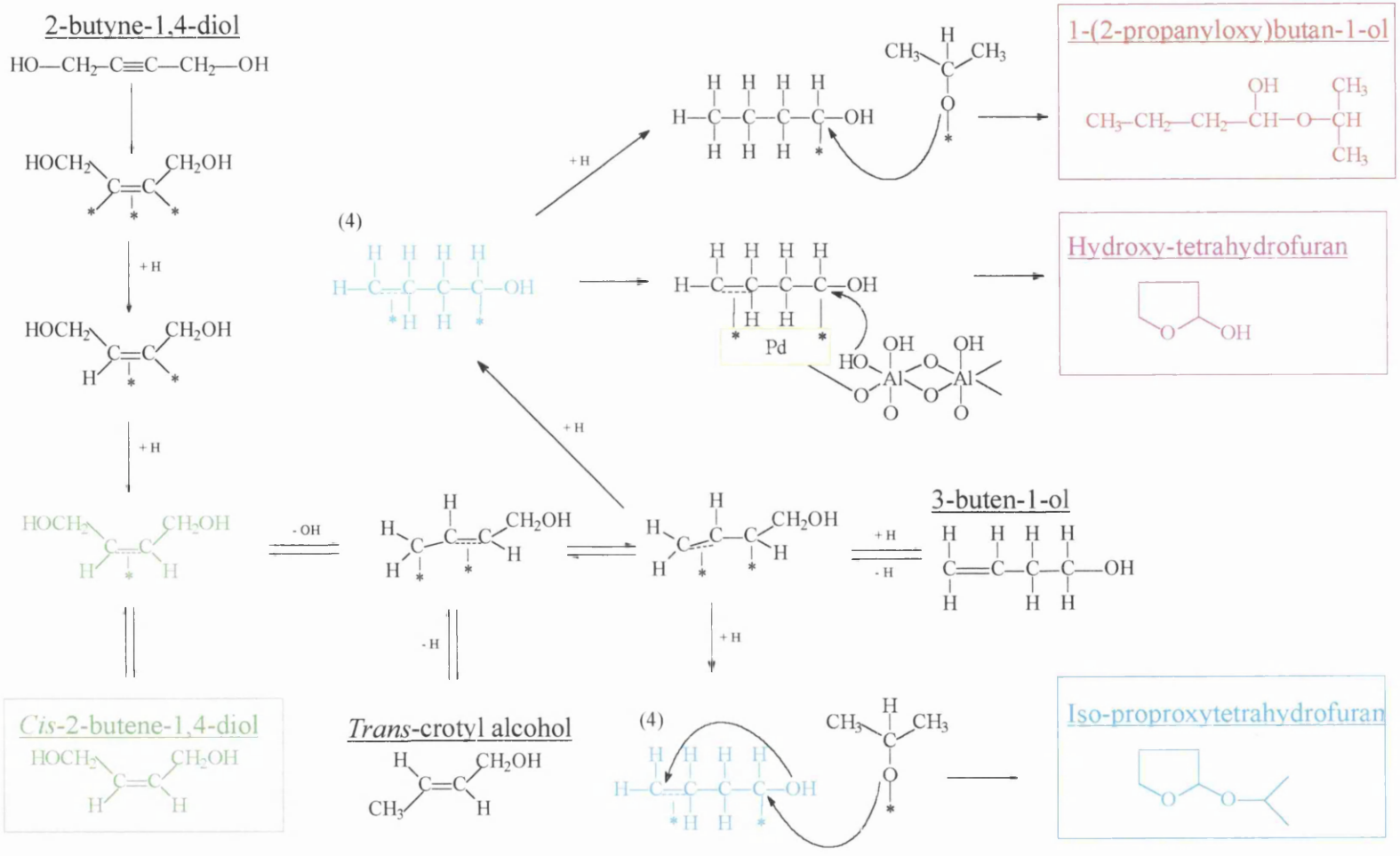


Figure 6.7.5: Reaction Mechanism part 4



Chapter Seven

CONCLUSIONS

7.1 The nature of palladium catalysts

i) BET studies show that the total surface areas for the catalysts change little from the original support.

ii) The dispersions for the 1% Pd/Al_2O_3 catalysts produced at Glasgow are considerably higher than the 1% Pd/C catalyst produced and supplied by Synetix

iii) The two 1% Pd/Al_2O_3 catalysts have considerably smaller metal particle sizes as determined by CO chemisorption and EM.

7.2 Ambient and elevated pressure reactions employing the 1% Pd/C catalyst

i) The ambient and elevated pressure batch slurry reactors were found suitable for the selective hydrogenation of 2-butyne-1,4-diol. The reaction could be used as a benchmark experiment to compare with other catalysts and reagents. The progress of the reaction could be followed by GC.

ii) The final product distributions for the elevated and ambient pressure reaction vessels were found to be essentially the same. The only exception to this was the production of 1-(2-propanyloxy)-butan-1-ol in the elevated pressure reaction vessel.

iii) Iso-propoxytetrahydrofuran was a major product in the final product distribution for both the ambient and elevated pressure reaction vessels that was unexpected. The only possible source for iso-propoxytetrahydrofuran was a solvent interaction. A similar mechanism can be attributed to the formation of 1-(2-propanyloxy)-butan-1-ol. The

formation of 1-(2-propanyloxy)-butan-1-ol can probably be attributed to the increased H concentration on the catalyst surface.

iv) There is little hydrogenation of *cis*-2-butene-1,4-diol when there is still 2-butyne-1,4-diol present in the reaction vessel. The "side products" come from *cis*-2-butene-1,4-diol rather than directly form 2-butyne-1,4-diol.

v) T.O.F. and hydrogenation rate increase with pressure from the ambient to elevated pressure reaction vessels.

vi) Reaction profiles, hydrogenation rates and final product distributions did not vary significantly when programmed and non-programmed reduction of the 1% Pd/C catalyst were compared. With the 1% palladium catalysts there was flexibility in the catalyst activation procedure.

vii) The blank test reactions showed there was no reaction when there was no catalyst present. There is no chance of any homogeneous reactions being responsibly for the production of any of the reaction products.

viii) Both the ambient and elevated pressure reactions vessels displayed selectivity in the order of 95% towards the formation of *cis*-2-butene-1,4-diol, up to 100% conversion of 2-butyne-1,4-diol.

ix) When *cis*-2-butene-1,4-diol was employed as the reaction reagent the selectivity was only in the order of 10% to butane-1,4-diol formation. The low selectivity to butane-1,4-diol formation when *cis*-2-butene-1,4-diol was employed as the reaction reagent mirrors the selectivity to butane-1,4-diol in the second stage of the reactions that employed 2-butyne-1,4-diol as the reaction reagent (100 to 200% conversion).

x) The mass-imbalance in the reactions that employed the 1% Pd/C catalyst was found to be due to butane and butene production, there was more production of butane and butene in the elevated pressure reaction vessel.

Butene and butane prevented a full mass balance being conducted for the reactions that employed the 1% Pd/C catalyst, due to their low solubilities in propan-2-ol.

7.3 Hydrogenation of 2-butyne-1,4-diol

i) The reaction is zero order with respect to 2-butyne-1,4-diol concentration, and zero order with respect to *cis*-2-butene-1,4-diol concentration.

ii) With reference to the literature it can be assumed that the reaction is first order with respect to $[H_2]$ The reaction may be expressed thus:-

iii) Rate = $d[A]/dt = k[Buty]^0 [H_2]^1 [cat]^1 [Bute]^0$ where k is a rate constant

iv) The value for the activation energy for 2-butyne-1,4-diol hydrogenation over palladium was found to be 37.05 ±1.4kJ/mole and 38.51 ±1.5kJ/mole for the 1% Pd/C and 1% Pd/Al_2O_3 catalysts respectively.

v) The rate of 2-butyne-1,4-diol hydrogenation was found to vary linearly with mass of catalyst, the reaction is first order with respect to catalyst mass.

vi) The initial concentrations of *cis*-2-butene-1,4-diol and 2-butyne-1,4-diol do not have any effect of the rate of 2-butyne-1,4-diol hydrogenation, hence the reaction is zero order with respect to *cis*-2-butene-1,4-diol and 2-butyne-1,4-diol concentration.

vii) The ambient pressure reaction vessel is under kinetic control, it is not diffusion limited, this indicates the validity of the ambient pressure reaction vessel as a means of evaluating different catalysts.

7.4 The 1% Pd/Al_2O_3 catalysts

i) Both the 1% Pd/Al_2O_3 catalysts show rate of hydrogenation of 2-butyne-1,4-diol that are considerably faster that those observed when the 1% Pd/C catalyst was employed.

ii) Both the 1% Pd/Al_2O_3 catalysts displayed different final product distributions when compared with the 1% Pd/C catalyst.

iii) With the two 1% Pd/Al_2O_3 catalysts the mass-balances were effectively complete. The reaction pathway to the formation of butene and butane are significantly retarded/unavailable when the 1% Pd/Al_2O_3 catalysts were employed.

iv) With the two 1% Pd/Al_2O_3 catalysts approximately double the amount of iso-propoxytetrahydrofuran was produced compared to when the 1% Pd/C catalyst was employed.

7.5 Continuous addition

i) There were effectively no mass balance problems with the continuous addition reaction, *i.e.* complete mass balance.

ii) While there is still 2-butyne-1,4-diol in the reaction vessel, *cis*-2-butene-1,4-diol production will continue with the suppression of the "side products"

iii) In Figure 5.6.1 more *cis*-crotyl alcohol was formed than *trans*-crotyl alcohol, this is the opposite of what had been observed in the reactions in Section 5.2. This increased formation may be due to increased residence time of the reaction intermediates on the catalyst surface.

7.6 Changing the reaction reagent

i) The diol functionality is required for the formation of iso-propoxytetrahydrofuran.

ii) 1-(2-propanyloxy)-butan-1-ol was produced instead of iso-propoxytetrahydrofuran, when the mono-substituted alkynes were employed as the reaction reagent. 1-(2-propanyloxy)-butan-1-ol is likely to be produced through a similar mechanism to iso-propoxytetrahydrofuran.

iii) The rate of reaction can be significantly effected by employing a reagent with the alkyne functionality in a different position.

iv) When the mono-substituted alkynes were employed as the reaction reagent, the mass-balances were more complete than those that employed 2-butyne-1,4-diol with the 1% Pd/C catalyst and propan-2-ol.

7.7 The 9.1% Cu/SiO_2 catalyst

i) The copper catalyst achieved a selectivity in the order of 98% to the formation of *cis*-2-butene-1,4-diol in the ambient pressure reaction vessel, and a selectivity in the order of 97% to the formation of butane-1,4-diol in the ambient pressure reaction vessel.

ii) There was no formation of iso-propoxytetrahydrofuran observed when the copper catalyst was employed.

iii) The range of "side products" produced with the copper catalyst was reduced.

iv) The reaction rate was considerably slower when the copper catalyst was employed when compared to the 1% Pd/C catalyst.

v) No activity was observed in any of the elevated pressure reactions that were attempted, further development of the reaction protocol for the elevated pressure reaction vessel employing a copper catalyst is required.

7.8 Replacement solvents

i) Employing water as a replacement solvent produces fewer "side products".

ii) Hydroxy-tetrahydrofuran was produced in the place of iso-propoxytetrahydrofuran when distilled was employed as the reaction solvent, butoxy-tetrahydrofuran was produced instead of iso-propoxytetrahydrofuran when butanol was employed as the reaction solvent. It is likely that if other different solvents are employed then other furan can be produced.

iii) The rate of hydrogenation when distilled water was employed as the reaction solvent was around half of that of a similar reaction that employed propan-2-ol as the reaction solvent, there is competition at the catalyst surface between 2-butyne-1,4-diol and water for adsorption. The mass-balances for the reactions that employed distilled water were effectively complete.

iv) Acid hydrolysis is not responsible for the formation of the "side products", in this study more acidic conditions (*i.e.* in distilled water rather than propan-2-ol) leads to the formation of less "side products".

7.9 Postulated reaction mechanism

i) A procedure was developed so that NMR and MS analysis analysis could be conducted of the reaction samples without disturbing the sample matrix.

ii) A combination of isotope switching and GC-MS combined with ^{1}H and ^{2}D NMR have been used to examine the reaction profile.

iii) The number of protons or deuterium atoms in each of the reaction species throughout the course of the reaction could be determined be a combination of MS and NMR.

iv) Combining previous experimental observation with the information gained using MS and NMR it is possible to propose a possible reaction mechanism that was entirely consistent with all the experimental observations.

7.10 FUTURE WORK

i) Further reaction testing with different solvents to see what other furans the adsorbed species/solvent interaction can produce. It has already been shown that butoxy-tetrahydrofuran and hydroxy-hydrofuran can be produced employing butanol and distilled water as the reaction solvent respectively.

ii) Reaction testing with longer chain and/or branched alkyne diols to see if higher membered rings and/or branched ring species can be produced.

iii) Further ^{1}H and ^{2}D isotope switching experiments to expand the postulated reaction mechanism to accommodate longer chained/branched alykyne diol starting species.

iv) Further optimisation of the reaction protocols for the 9.1% Cu/SiO_2 catalyst, to achieve enhanced activity in the ambient pressure reaction vessel, and activity in the elevated pressure reaction vessel.

REFERENCES

REFERENCES FOR CHAPTER 1

1. J.W. Dobereiner, J. Chem. Phys., 38 (1823) 321

2. S.J. Gregg and K.S.W. Sing, 'Adsorption, Surface Area and Porosity', Academic Press, New York, 1967, references therein

3. R.J. Farrauto and C.H. Bartholomew, 'Fundamentals of Industrial Catalytic Processes', Blackie Academic & Professional, New York, 1997, p3

4. C.N. Satterfield, 'Heterogeneous Catalysis in Industrial Practice', McGraw-Hill Inc., New York 1991, p8

5. B.C. Gates, 'Catalytic Chemistry', John Wiley & Sons, New York, 1992

6. P.N. Rylander, 'Hydrogenation Methods', Academic Press, London, 1985, (a, p1) (b, chapters 2 and 3)

7. G.A. Somorjai, 'Introduction to Surface Chemistry and Catalysis', Wiley-Interscience, New York, 1994, p455

8. M.V. Twigg, 'Catalyst Handbook', 2nd Ed., Manson Publishing, London, 1996, p23

9. A. Molnar, A. Sarkany and M. Varga, J. Mol. Catal. A: Chem., **173** 2001 185

10. H. Lindar and R. Dubuis, Org. Syn., **46** (1996) 89

11. S. Siegel, Adv. Catal., **16** (1966) 160

12. D. Kennedy, PhD Thesis, University of Glasgow, (1997)

13. M. Derrien, in 'Catalytic Hydrogenation', ed. L. Cerveny, Elsevier, Amsterdam, 1986, p613

14. L. Kniel, O. Winter and K. Stark, 'Ethylene: Keystone to the Peterochemical Industry', Marcel Dekker, New York, 1980.

15. W. Weirauch, Hydro. Pro., 77 (9) (1998) 25

16. P.E. Bagget, Pet. Tech. Quart., (1998) 7

17. S. Zehnder, Hydro. Pro., 77 (2) (1998) 59

18. E.N. Marvell and T. Li, Synthesis (1973) 457

19. G. Webb, in 'Specialist Periodical Reports Catalysis Volume 2', (Senior Reporters) C. Kemball, and D.A. Dowden, The Chemical Society, 1978, p145

20. D. Parker, in 'The Chemistry of Functional Groups. The Chemistry of the Metal-Carbon Bond', Vol. 4, ed. F.R. Hartley, Wiley, Chichester, 1987, chapter 11

21. S. Siegel, in 'Comprehensive Organic Synthesis', Vol. 8: Reduction, eds B.M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, p417

22. R.L. Augustine, 'Heterogeneous Catalysis for the Synthetic Chemist', Marcel Dekker, New York, 1996, chapters 15 and 16

23. M. Bartok and A. Molnar, in 'The Chemistry of Functional Groups. Supplement A3: The Chemistry of Double-Bonded Functional Groups', ed S. Patai, Wiley, Chichester, 1997, p876

24. H. Arnold, F. Dobert and J. Gaube, in 'Handbook of Heterogeneous Catalysis', eds G. Ertl, H. Knozinger and J. Weitkamp, VCH, Weinheim, 1997, p2165

25. G.V. Smith and F. Notheisz, 'Heterogeneous Catalysis in Organic Chemistry', Academic Press, San Diego, 1999, chapter 2

26. A.N.R. Bos and K.R. Westerterp, Chem. Eng. Pro., **32** (1993) 1

27. P.N. Rylander, 'Catalytic Hydrogenation over Platinum Metals', Acedemic Press, New York, 1967, chapters 4 and 5

28. P.N. Rylander, 'Catalytic Hydrogenation in Organic Syntheses', Academic Press, New York, 1979, chapters 2 and 3

29. H. Pines, 'The Chemistry of Catalytic Hydrocarbon Conversions', Academic Press, New York, 1981, chapter 3

30. M. Bartok, J. Czombos, K. Felfoldi, L. Gera, G. Gondos, A. Molnar, F. Notheisz, G. Wittmann and A. Zsigmond, 'Sterochemistry of Heterogeneous Metal Catalysis', Wiley, Chichester, 1985, chapters 3 and 4

31. A.S. Al-Ammar and G. Webb, J. Chem. Soc. Farad. (I), **75** (1979) 1900

32. S. Asplund, C. Fornell, A. Holmgren and S. Irandoust, Cat. Today, **24** (1995) 181

33. S. Asplund, J. Catal., **158** (1996) 267

34. J.U. Reid, S.J. Thomson and G. Webb, J. Catal., **30**, (1973) 378

35. J.U. Reid, S.J. Thomson and G. Webb, J. Catal., **30**, (1973) 372

36. C.M. Pradier, M. Mazina, Y. Berthier and J. Oudar, J. Mol. Catal., **89** (1994) 211

37. J.M. Moses, A.H. Weiss, K. Matusek and L. Guczi, J. Catal., **86** (1994) 417

38. G.C. Bond and J. Sheridan, Trans. Farad. Soc., **48** (1952) 651

39. R.S. Mann and K.C. Khulbe, J. Phys. Chem., **73** (1969) 2104

40. S.D. Jackson and G. Kelly, J. Mol. Catal., **87** (1994) 275

41. S.D. Jackson and N.J. Casey, J. Chem. Soc. Farad. Trans., **91**(18) (1995) 3269

42. Ph. Maetz and R. Touroude, J. Mol. Catal., **91** (1994) 259

43. J.P. Boutiaux, J. Cosyns and E. Robert, Appl. Catal., **35** (1987) 193

44. W.M. Hamiltom and R.L. Burwell, Proc. 2nd Intern. Congr. Catal., Paris, (1960), p987; (1961), Technip, Paris

45. E.F. Meyer and R.L. Burwell, J. Am. Chem. Soc., **85** (1963) 2877

46. G. Webb and P.B. Wells, Trans. Farad. Soc., **61** (1965) 1232

47. J. Hagen, 'Industrial Catalysis: A Practical Approach', Wiley-VCH, Chichester, 1999, p308

48. J.A. Godfrey and R.A. Searles, Chemie-Technik **10**(12) (1981) 1271

49. J.B.F. Anderson, K.G. Griffin and R.E. Richards, Chemie-Technik **18**(5) (1989) 40

50. J.M. Winterbottom, H. Marwan, J. Viladevall and S. Sharma, Het. Catal. And Fine Chem., **IV** (1997) 59

51. G.C. Bond, G. Webb, P.B. Wells and J.M. Winterbottom, J. Catal. **1** (1962) 74

52. R. Del Rosso, C. Mazzochia, P. Gronchi and P. Centola, Appl. Catal., **9** (1984) 269

53. J.M. Campelo, R. Guardeño, D. Luna and J.M. Marinas, J. Mol. Catal. **85** (1993) 305

54. L.K. Freidlin and Z. Balandin, Dokl. Acad. Nauk. SSSR, **124** (1959) 598

55. F. Turek and H. Winter, Ind. Eng. Chem. Res., **29** (1990) 1546

56. J.A. Monick, in,'Alocohols', General Aniline and Film Corp., Reinhold, New York, 1962

57. E.V. Host, US Patent, 2 953 604 (1960)

58. R.V. Chaudhari, M.G. Paranede, P.A. Ramachandran, P.H. Brahme, H.G. Vadgaonkar and R. Jaganthan, AIChE., **31**(11) (1985) 1891

59. R.V. Chaudhari, R. Jaganthan and D.S. Kolhe, Appl. Catal., **29** (1987) 141

60. M.M. Telkar, C.V. Rode, V.H. Rane, R. Jaganathan and R.V. Chaudhari, Appl. Catal. A., **216** (2001) 13

61. T.W. Russel and D.M. Duncan, J. Org. Chem. **39** (1974) 3050

62. R.J. Tedeschi, H.C. McMahon and M.S. Pawlak, Annals New York Academy of Sciences, **145** (1967) 91

63. F.J. McQuillin and W.O. Ord, J. Chem. Soc., (1954) 2902

64. I. Jardine, R.W. Howsam and F.J. McQuillin, J. Chem. Soc. (C)., (1969) 260

65. T. Fukuda, Bull. Chem. Soc. Japan., **31** (1958) 343

66. T. Fukuda and T. Kusuma, Bull. Chem. Soc. Japan., **31** (1958) 339

67. A.W. Johnson, J. Chem. Soc., **68** (1946) 1014

68. T. Suwa, Jap. Patent 3417 (1956)

69. A.S. Wood and J.M. Reitz, Germ. Offen., 2 605 241 (1976)

70. H. Hofmann, G. Boettger, K. Boer, W. Wache, H. Grafje and W. Koerning, Germ. Offen., 2 451 929 (1976)

71. P.W. Feit, Chem. Bl., **93** (1960) 116

72. W.Reppe, Chem. Ing. Technik, 24/24, (1950) 527

73. D. I. MaGee, J. D. Leach and S. Setiadji, Tetrahedron, **55** (1999) 2847

74. B. Trost and J. Flygare, J. Org. Chem., J. Org. Chem., **59** (1994) 1078

75. A.A. Look, M.T. Burch, W. Fenical, Z. Qi-Tai and J. Clardy, J. Org. Chem., **50** (1985) 5741

76. T. Tsai, H. Jin and K. Wiesner, Can. J. Chem., **62** (1984) 1403

77. S. Woo and B. Keay, Tetrahedron: Asymmetry, **5** (1994) 1411

78. D. I. MaGee and J. D. Leach, Tet. Let., **38** No. 8 (1997)

79. B. Gabriele, Tet. Lett., **40** (1999) 989

80. C. D. Brown and J. M. Chong, Tet. Let., **55** (1999) 14233

81. D. I. Magee and J. D. Leach, Tet. Let., **38** No. 47 (1997) 8219

82. H. E. Burdick and H. Adkins, J. Amer. Chem. Soc., **56** (1934) 438

83. N. I. Chouikine and I. F. Belsky, Actes Cong. Intern. Catalyse, 2nd, Paris, 1960 (1961) **2** 2625

84. S. D. Jackson and J. Huntingdon, Catal. Deact., (1999) 453

85. C. Godawa and A. Gaset, J. Mol. Catal., **34** (1986) 199

86. A. D. Shebaldova and L. A. Safronova, Rus. J. Gen. Chem; **66**(1) (1996) 109

REFERENCES FOR CHAPTER 3

87. D. Anderson, PhD Thesis, University of Glasgow, (1999)

88. D.B. Williams, C. Barry Carter, 'Transmission Electron Microscopy', Plenum Press, New York, 1996, Vol.1, p142

REFERENCES FOR CHAPTER 5

1. D. Anderson, PhD Thesis, University of Glasgow, (1999)

2. D. Kennedy, PhD Thesis, University of Glasgow, (1997)

3. J.L. Lemaitre, P.G. Menon and F. Delannay, in 'Characterisation of Heterogeneous Catalysts", (F. Delannay, Ed.), Chemical Industries/15, Marcel Dekker, New York, (1994), p299-365

4. J.S. Smith, P.A. Thrower and M.A. Vannice, J. Catal., **56** (1979) 236

5. A.P. Boyes, X.X. Lu, S. Raymahasay, S. Saremento, M. W. Tilston and J.M. Winterbottom, Trans. IChemE., **69** (1991) 201

6. A. P. Boyes, A. Chughtai, X.X. Lu, , S. Raymahasay, S. Saremento, M. W. Tilston and J.M. Winterbottom, Chem. Eng. Sci., **47**(13/14) (1992) 3729

7. A. P. Boyes, A. Chughtai, Z. Khan, S. Raymahasay, A.T. Sulidis and J.M. Winterbottom, J. Chem. Tech. Biotechnol., **64** (1995) 55

8. M. Lanier, M. Haddach, R. Pastor and J.G. Reiss, Tet. Let. (1993) 2469

9. J.M. Winterbottom, H. Marwan, J. Viladevall and S. Sharma, Het. Catal. And Fine Chem., **IV** (1997) 59

10. I. Duncanson, PhD Thesis, University of Glasgow, (Aug 2001), (work in progress)

11. T. Ouchaib, J. Massardier and A. Renouprez, J. Catal. **119** (1989) 517

12. X.C. Guo and R.J. Madix, J. Catal. **155** (1995) 336

13. P. Sautet and J.F. Paul, Catal. Lett. **9** (1991) 245

14. L. Cerveny, Catal. Rev.-Sci. Eng. **24** (1982) 503

15. L. Cerveny, Chem. Eng. Commun. **83** (1998) 31

16. W.T. Tysoe, G.L. Nyberg, R.M. Lambert, J. Chem. Soc., Chem. Commun. (1983) 623

17. Z. Dobrovolna. P. Kacer and L. Cerveny, J. Mol. Catal. A:Chem. **130** (1998) 279

18. J. Hagen, 'Industrial Catalysis: A Practical Approach', Wiley-VCH, Chichester, 1999, p93

19. J.M. Campelo, R. Guardeño, D. Luna and J.M. Marinas, J. Mol. Catal., **85**, (1993) 305

20. M.M. Telkar, C.V. Rode, V.H. Rane, R. Jaganathan and R.V. Chaudhari, Appl. Catal. A., **216** (2001) 13

21. R.V. Chaudhari, M.G. Paranede, P.A. Ramachandran, P.H. Brahme, H.G. Vadgaonkar and R. Jaganthan, AIChE., **31**(11) (1985) 1891

22. R.V. Chaudhari, R. Jaganthan and D.S. Kolhe, Appl. Catal., **29** (1987) 141

23. T. Fukuda, Bull. Chem. Soc. Japan., **31** (1958) 343

24. T. Fukuda and T. Kusuma, Bull. Chem. Soc. Japan., **31** (1958) 339

25. G.C. Bond, 'Heterogeneous Catalysis: Principles & Applications', Clarendon Press, Oxford, 1974, (a, p82), (b, p49)

26. J.H. Espenson, 'Chemical Kinetics and Reaction Mechanisms' McGraw-Hill Book Company, New York, 1981, p5

27. R.S. Farranto and C.H. Bartholomew, 'Fundamentals of Industrial Catalytic Processes', Blackie Academic and Professional, London, 1997, p18

28. J.M. Coulson and J.F. Richardson, 'Chemical Engineering', Pergamon Press, Oxford, Vol. 2, 1983, p86

29. P.W. Atkins, 'Physical Chemistry', Oxford University Press, Oxford, 1994, p220

30. C.N. Satterfield, 'Heterogeneous Catalysis in Industrial Practice,' Krieger Publishing Company, Florida, 1991, p479-483

31. J.M. Thomas and W.J. Thomas, 'Principals and Practice of Heterogeneous Catalysis', VCH, Cambridge, 1997, p477

32. K. Klier, Adv. Catal., **31** (1982) 243

33. H.H. Kung, Catal. Rev.-Sci. Eng., **22** (1980) 235

34. G.C. Chinchen, P.J. Denny, J.R. Jennings, M.S. Spencer and K.C. Waugh, Appl. Catal., **36** (1988) 1

35. J. Jenck and J.E. Germain, J. Catal., **65** (1980) 141

36. R. Hubaut, J.P. Bonnelle and M. Daage, J. Mol. Catal., **55** (1989) 170

37. R. Del Rosso, C. Mazzochia, P. Gronchi and P. Centola, Appl. Catal., **9**, (1984) 269

38. T.M. Meulemans, N.H. Kiers, B.L. Feringa and P.W.E.M. van Leeuwen, Tet. Let., **35**, (1994) 455

39. N. Nojira and M. Misono, Appl. Catal. A, **93** (1993) 108

40. J.I. Kroschwitz and M. Howe-Grant, 'Encyclopedia of Chemical Technology', John Wiley & Sons, Vol. 2, 4th ed, 1992, p146

41. C.U. Pittman and W.D. Honnick, J. Org. Chem. **45** (1980) 2132

42. M. Matsumoto and M. Tamura, US Patent 4 356 333 (1982)

43. Y. Harano, US Patent 4 465 873 (1984)

44. M. Matsumoto, S. Miura, K. Kikuchi, M. Tamura, H. Kojima, K. Koga and S. Yamashita, US Patent 4 567 305 (1986)

REFERENCES FOR CHAPTER 6

1. J.M. Winterbottom, H. Marwan, J. Viladevall and S. Sharma, Het. Catal. And Fine Chem., **IV** (1997) 59

2. R.V. Chaudhari, R. Jaganthan and D.S. Kolhe, Appl. Catal., **29** (1987) 141

3. R. Del Rosso, C. Mazzochia, P. Gronchi and P. Centola, Appl. Catal., **9** (1984) 269

4. M.M. Telkar, C.V. Rode, V.H. Rane, R. Jaganathan and R.V. Chaudhari, Appl. Catal. A., **216** (2001) 13
5. I. Jardine and F.J. McQuillin, J. Chem. Soc., (C), (1966) 458

6. R. Tedeschi, J. Org. Chem., **27** (1962) 2398

7. P.N. Rylander, L. Hasbrouck, S.G. Hindin, R. Iverson, I. Karpenko and G. Pound, Engelhard Ind., Tech. Bull., **8**(3) (1967) 93

8. T.M. Meulemans, N.H. Kiers, B.L. Feringa and P.W.E.M. van Leeuwen, Tet. Let., **35**, (1994) 455

9. C.J. Ponchert and J. Behnke, 'The Aldrich Library of ^{13}C and ^{1}H FT NMR spectra', Aldrich Chemical Company, 1993 (a, p514, C, volume 3), (b, p221, A, volume 1), (c, p195, B, volume 1), (d, p164, A, volume 1), (e, p208, A, volume 1), (f, p208, B, volume 1)

10. D. Kennedy, PhD Thesis, University of Glasgow, (1997)

11. G. Webb, 'Specialist Periodical Reports Catalysis Volume 2', The Chemical Society, 1978, p145

12. M.A. Chesters, J. Mol. Struct. **173** (1998) 405

13. M.A. Chesters and E.M. McCash, J. Electron Spectrosc. Relat. Phenom., **44** (1987) 99

14. A. Frick, H. Graupwer, L. Hammer and K. Muller, Surf. Sci., **277** (1992) 182

15. M.A. Chesters, C. De La Cruz, P. Gardner, E. M. McCash, P. Pudney, G. Shahid and N. Sheppard, J. Chem. Soc. Farad. Trans., **80** (15), (1990) 2757

16. N.R. Avery and N. Sheppard, Surf. Sci., **169** (1986) L367

17. J.P. Camplin, J.K. Eve and E.M. McCash, Phys. Chem. Chem. Phys. **2** (2000) 4433

18. K. Klier, Adv. Catal., **31** (1982) 243